THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Excess heat utilisation in oil refineries – CCS and algae-based biofuels

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2016

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GÖTEBORG, 2016
ISBN-978-91-7597-452-1

Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 4133
ISSN 0346718X

Publication 2016:2
Industrial Energy Systems and Technologies
Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY, GÖTEBORG
ISSN 1404-7098

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Front cover: Photo by Preem
Back cover: Photo by Jan-Olof Yxell

Printed by Chalmers Reproservice
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2016

This thesis is based on work conducted within the interdisciplinary graduate school Energy Systems. The national Energy Systems Programme aims at creating competence in solving complex energy problems by combining technical and social sciences. The research programme analyses processes for the conversion, transmission and utilisation of energy, combined together in order to fulfil specific needs.

The research groups that participate in the Energy Systems Programme are the Department of Engineering Sciences at Uppsala University, the Division of Energy Systems at Linköping Institute of Technology, the Department of Technology and Social Change at Linköping University, the Division of Heat and Power Technology at Chalmers University of Technology in Göteborg as well as the Division of Energy Processes at the Royal Institute of Technology in Stockholm.

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ABSTRACT

The main objective of this thesis is to investigate two different concepts for CO_2 mitigation, from a system perspective, in relation to the oil refining industry: CO_2 capture and storage; and algae-based biofuels. For all these processes, process integration with an oil refinery is assumed. The oil refinery sector is a major emitter of CO_2 and is responsible for 9% of the industrial emissions of CO_2 worldwide. Oil refineries have large amounts of unused excess heat, which can be used to satisfy the heat demands of a CO_2 capture plant, a land-based algal cultivation facility, or an algae-based biofuel process. The use of this excess heat significantly reduces the cost for CO_2 capture, while an economic evaluation for algae-based biofuels has not been made.

Since the amount of heat available from the oil refinery´s processes increase with decreasing temperature in the stripper reboiler, it was investigated how much heat was available at different temperatures. It was also investigated how the decreased temperature would affect the heat demand of CO_2 capture processes that use MEA or ammonia as the absorbent. The findings show that it is possible to capture more CO_2 using excess heat when the temperature in the stripper reboiler is decreased. For the MEA process, the lower limit of the temperature interval investigated showed the maximum CO_2 capture rate, while the ammonia process benefitted from a lower temperature than the standard temperature but showed maximal CO_2 capture rate above the lower limit. These results are valid only when using excess heat to satisfy the entire heat demand. At the case study refinery, the available excess heat could satisfy between 28% and 50% of the heat demand of the MEA process when treating the flue gases from all chimneys, depending on the temperature in the stripper reboiler. This utilisation of excess heat represents a way to reduce significantly the costs for CCS in an oil refinery.

Land-based cultivation of algae proved to be unsuitable for the utilisation of excess heat. Since the cultivation pond is exposed to wind, rain, and cold, the heat demand fluctuates strongly over the year, making the pond an unstable recipient of the excess heat.

Three types of biofuel processes based on microalgae and macroalgae were investigated with respect to integration with the oil refinery. For the algae-based biofuel processes, heat integration and material integration combined to increase the efficiency of the system. When two different build margin technologies (with different CO_2 emission factors) are employed for electricity production, macroalgae-based biofuel production appears to be the more robust process from the perspective of CO_2 due to the lower electricity demands of the algal cultivation and harvesting phases.

Keywords: CO_2 emissions, GHG emissions, carbon dioxide, process integration, post-combustion, carbon capture and storage (CCS), oil refining industry, techno-economic, algae biofuels, renewable diesel.

Appended papers

This thesis is based on the work described in the following papers. The papers are not listed in chronological order based on date of publishing, but rather in the order that makes it easier for the reader to follow the structure of this thesis.

I. Industrial excess heat driven post-combustion CCS: The effect of stripper temperature level
Andersson V, Franck P-Å, Berntsson T (2014)
International Journal of Greenhouse Gas Control, 21, 1–10

II. Efficient utilization of industrial excess heat for absorption-based CO_2 capture:
Andersson V, Normann F, Franck P-Å, Berntsson T
Submitted to International Journal of Greenhouse Gas Control (2016)

III. Techno-economic analysis of post-combustion CCS at an oil refinery
Andersson V, Franck P-Å, Berntsson T (2016)
International Journal of Greenhouse Gas Control, 45, 130–138

IV. Algae-based biofuel production as part of an industrial cluster
Andersson V, Broberg S, Hackl R, Karlsson M, Berntsson T (2014)
Biomass and Bioenergy, 71, 113-124

V. Comparison of three algae-based biofuel routes and the possibilities for process integration with an oil refinery, Andersson V, Heyne S, Berntsson T
Submitted to Biomass and Bioenergy (2016).

Co-authorship statement

Viktor Andersson has been the main author of **Papers I-III and V**. **Paper IV** was co-authored with Sarah Broberg and Roman Hackl. Viktor Andersson was responsible for the cultivation heat balances, biodiesel production processes, and utilisation of excess heat, while Sarah Broberg was responsible for the biogas process, and Dr. Roman Hackl was responsible for the algae cultivation in regard to wastewater treatment, nutrients, and harvesting. Professor Thore Berntsson supervised the work in all papers. Dr. Per-Åke Franck co-supervised the work in **Papers I-III**. Dr. Fredrik Normann co-supervised the work in **Paper II** while Dr. Stefan Heyne co-supervised the work in **Paper V**. Dr. Henrik Jilvero has done the process simulations for the ammonia process in **Paper II**.

Related work not included in this thesis

- Temperature dependence of heat integration possibilities of an MEA scrubber plant at a refinery
  Andersson, V., Franck, P-Å., Berntsson, T. (2013)
  Energy Procedia, 37, 7205-7213
  (This paper is a conference version of **Paper I**)

- Efficient utilization of industrial excess heat for post-combustion CO_2 capture: An oil refinery sector case study
  Andersson, V., Jilvero, H., Franck, P-Å., Normann, F., Berntsson, T. (2014)
  Energy Procedia, 63, 6548-6556
  (This paper is a conference version of **Paper II**)

- Integrated algae cultivation for municipal wastewater treatment and biofuels production in industrial clusters
  Andersson, V., Broberg, S., Hackl, R. (2012)
  World Renewable Energy Forum, WREF 2012, Including World Renewable Energy Congress XII and Colorado Renewable Energy Society (CRES) Annual Conference 1, pp. 684-691
  (This paper is a conference version of **Paper IV**)

- Integrated Algae Cultivation for Biofuels Production in Industrial Clusters
  Andersson, V., Broberg, S., Hackl, R. (2011)
  Working paper no. 47, Energy Systems Programme (This publication is a pre-study for **Paper IV**)

Table of contents

1 Introduction

This chapter begins with a short introduction to the thesis. . The chapter continues with the objective of the thesis and a description of the research questions posed, and it ends with an overview of the appended papers.

This thesis investigates two possibilities for a more sustainable oil refinery sector: carbon capture and storage (CCS); and algae-based biofuels. The options are inherently different, in that CCS targets the oil refinery processes *per se* while algae biofuels are directed towards the emissions in the fuel. The fact that the options are inherently different also enables the possibility of performing biomass-based CCS.

Neither of the two options are currently considered to be economically feasible. While CCS is in the demonstration phase with projects that are up and running, algae-based biofuels remain in the conceptual phase. Thus, it is very difficult to investigate the whole algae biofuel chain from a techno-economical perspective at the present time.

1.1 Background

In 1997, the Kyoto protocol was signed, whereby 38 countries established their intent to decrease their greenhouse gas emissions (GHG, in CO_2 equivalents, hereafter termed 'CO_2 emissions') relative to their CO_2 emissions levels in 1990. In 2015, the Paris Agreement was drawn up, in which all countries have binding targets "*holding the increase in the global average temperature to well below 2 °C above pre-industrial levels, recognizing that this would significantly reduce the risks and impacts of climate change*". As of July 2016, 20 parties have ratified the Paris Agreement, accounting for 0.4% of global CO_2 emissions ("The Paris Agreement - main page," 2016). While it is still too early to evaluate the Paris Agreement, the Kyoto protocol can be evaluated as it ended its first commitment period on December 31, 2012 (Shishlov et al., 2016). In their study, Shishlov et al. (2016) analysed *ex post* the extents of compliance of the 38 countries that were signatories to the protocol. Of these 38 countries, the USA eventually did not ratify the protocol, and Canada abandoned the protocol in Year 2011. At the end of the first commitment period, the 36 countries that fully participated in the Kyoto protocol had decreased their CO_2 emissions by 24% compared to their base year, thereby surpassing the target by 2.2 Gt_{CO2}/y. Even if the USA and Canada are included in the analysis, the target is surpassed. This engenders optimism for the new agreement.

Since future CO_2 emissions levels are impossible to predict with precision, the International Energy Agency (IEA) has developed three different scenarios in their annual publication, the World Energy Outlook (WEO) (IEA/OECD, 2013), two of which have been included

in the calculations in this thesis. The scenarios include assumptions (regarding governmental policies and measures) that are used throughout this thesis and that are described in detail in Section 4.5.

This thesis is a continuation of the work previously carried out at the Division of Industrial Systems and Technologies (the division formerly known as the Division of Heat and Power Technology) at Chalmers University of Technology by, for instance, Hektor (2008) and Johansson (2013) with the general goal of comparing CCS with algae-based biofuel production.

1.2 The oil refinery sector

The oil refinery sector is currently facing multiple challenges, as the CO_2 emissions from refineries must decrease at the same time as the regulations for energy-demanding sulphur removal have increased (Fonseca et al., 2008). Meanwhile, the fuel mix should shift towards an increasing share of biomass-based fuels. As presented in Figure 1, oil refining-related emissions amount to 9% of the total industrial CO_2 emissions. The whole industrial sector emits 16 $GtCO_2$ annually, plus 0.89 Gt of non-CO_2 GHG emissions.

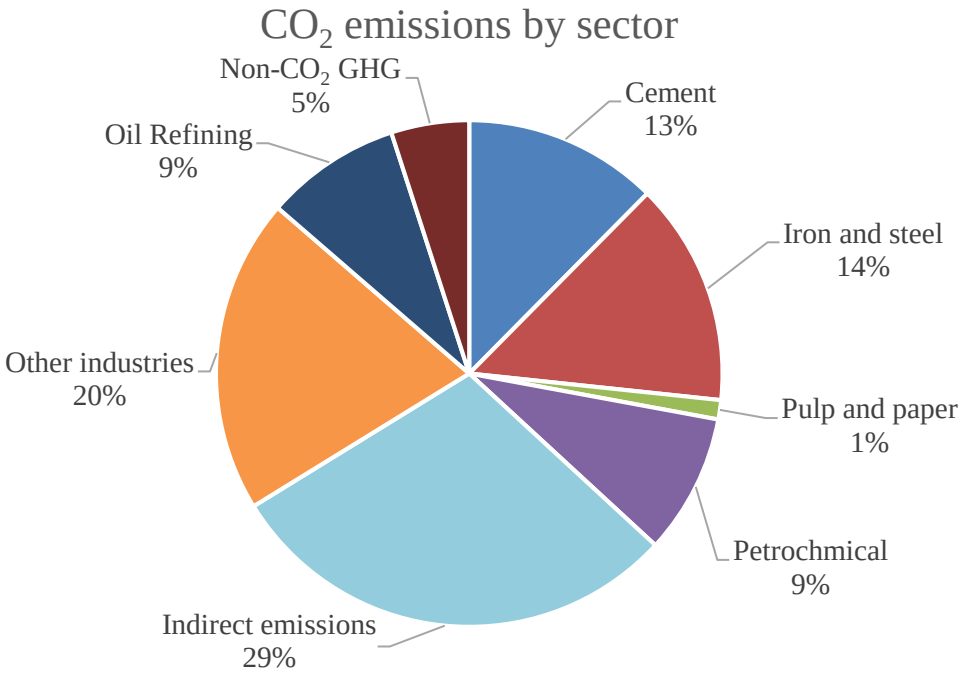

Figure 1: Yearly CO_2 emissions from the industrial sector.

A breakdown of the emissions from refineries globally shows that 65% of the CO_2 emitted originates from furnaces and boilers (Kuramochi et al., 2012). Around 4%–15% of the crude oil input of a refinery is used for process energy transformation (Szklo and Schaeffer, 2007), and it can be argued that of the total emissions that arise from petroleum products, the share from refining is also 4%–15%. The remaining fraction of the CO_2 emissions (85%–96%) originates from vehicles that are driven by the oil products. This emphasises the need for a change of feedstock.

DNV GL (2015) lists enablers of and barriers to the decarbonisation of oil refineries. Many of the enablers are so-called "sticks", and only a willingness on the part of the management to make climate change a priority can really be characterised as a "carrot". This stands in bright contrast to the findings of CONCAWE (2013) which predicts a decrease of approximately 25%–30% in the demand for traditional refinery products between Year 2005 and Year 2030. Of this decrease, 23% is due to the penetration of alternative road fuels. If such a high percentage of the traditional products will be replaced by newer fuels, it would make sense to adapt the refinery to start producing these new fuels, so as to ensure competitiveness; a "carrot" situation. This is one of the main reasons why the oil refinery sector is becoming increasingly interested in biomass-based products.

There are three main categories of measures for CO_2 mitigation (IPCC, 2007):

- Energy efficiency
- Carbon capture and storage (CCS)
- Low-carbon energy sources

In this thesis, the main work has focused on CCS, and the emerging concept of switching from fossil feedstock to biofuels, in this case algae-based biofuels.

1.3 Carbon capture and storage

The underlying idea with CCS processes is to obtain a pure stream of CO_2 (CO_2 capture), transport it under high pressure to a location, and then dispose/transform it. There are in principle four technology options for CO_2 capture:

- Pre-combustion processes: Hydrogen and CO_2 are produced from the fuel before combustion, thereby creating the opportunity to combust the hydrogen without the formation of CO_2.
- Post-combustion processes: The fuel is combusted as normal, and the CO_2 is subsequently removed from the flue gases. When no fuel is combusted (i.e., in hydrogen production) this option is named after the chemical unit of transformation, e.g., adsorption-based or absorption-based processes.
- Oxyfuel combustion: An air separator separates the oxygen from the combustion air, and the fuel is combusted in pure oxygen. This results in a pure CO_2 stream as an off-gas. Flue gases can also be recirculated to the inlet of the boiler for easier control of the process.
- Chemical-looping combustion: An oxygen carrier (e.g., metal slab) transports the oxygen to a fluidised bed where combustion takes place. The CO_2 exits the fluidised bed as a pure stream. This technology is, however, still at the pilot scale.

CO_2 capture can be implemented in the industrial and power sectors, although there are significant differences between these two sectors. The main differences are the levels of emissions, the CO_2 concentrations in the flue gases, and the fact that industrial plants often have access to significant amounts of excess heat at low or medium temperature. An oil refinery can have CO_2 at concentration that range from 1% to 50%; a coal-fired power plant

typically has 14% CO_2. Whereas the chimneys at a power plant are centralised, the chimneys at an industrial plant are typically scattered over the site. The excess heat can be used to cover parts of the heat demand, since the absorption-based CO_2 capture techniques in particular are associated with a high demand for heat.

There are two alternatives for the transportation of CO_2:

- Ship
- Pipeline

The preferred option depends on the mass flow of CO_2 and the distance from the source to the sink, and both methods have advantages and disadvantages. Shipping has a lower capital cost but a higher operational cost than using a pipeline; ships are more flexible but have a greater need for onshore installations (Skagestad et al., 2014).

Storage is the most uncertain step of the process. Two (main) storage possibilities have been proposed:

- Mineralisation, whereby the CO_2 reacts to form a solid material that can be used to form value-added materials (Werner et al., 2014).
- Pumping the CO_2 down a borehole deep underground, either below the land or below the ocean (Bachu, 2000).

The latter idea is the most intensively researched to date, due to the greater challenges posed by the other the techniques. However, pumping the CO_2 into a borehole also has its challenges, mainly related to characterising the storage site. The ideal storage site is porous rock with a "cap rock" on top to prevent the CO_2 from leaking, e.g., abandoned oil and gas fields, and aquifers (Bachu, 2000). The proposal to store the CO_2 below land has spawned considerable debate and resistance locally at the storage sites, while storage deep under the seabed is more socially acceptable.

This thesis focuses exclusively on absorption-based processes in the oil refinery sector, and investigates the capture part of the CCS chain.

1.4 Algae-based biofuels

Research into methods for producing algae on a large scale for biomass feedstock can be traced back several decades. At that time, it was mostly studied in the USA, and algae-based power generation was cost-comparable with nuclear power (Oswald and Golueke, 1960). The easiest way of producing fuel from algae (and the first to be explored) is to digest it into biogas (Golueke et al., 1957). Since then, however, several other fuels have been produced by algae, including fatty acid methyl esters (FAME, also known as biodiesel), bioethanol, biohydrogen, and biobutanol (Berlin et al., 2013). There are two main types of algae, which differ in composition and size, microalgae and macroalgae. In this thesis, a comparison of the two main categories of algae is made.

Algae-based biofuels are considered to be third-generation biofuels (Lee and Lee, 2016). First-generation biofuels, such as ethanol from wheat, biogas from corn, and biodiesel from rapeseed oil, have been criticised for their low land-use efficiency, increasing pressure on arable land, and their poor carbon balance. The production of first-generation biofuels has been linked to increased emissions and rising food prices. Several studies have examined the complexity and controversy surrounding the use of food biomass for biofuels (Mitchell, 2008; Searchinger et al., 2008; Timilsina et al., 2012). The second-generation biofuels use lignocellulosic materials, jathropa, and other non-food crops, to (for example) gasify black liquor or to produce ethanol and Fischer–Tropsch diesel (Sims et al., 2010). The difference between the generations of biofuels lie not mainly in the processes, but rather in the feedstocks used (Alaswad et al., 2015). The variety of available feedstocks raises the need for *ex ante* evaluations to identify early the pathways and the research need.

1.5 Objective

The objective of this PhD thesis has been to illustrate different pathways to a more sustainable oil refinery sector. Based on this objective, this thesis can be divided into the following research questions:

Q1. In an industrial process with access to excess heat, how can this heat be used to create a lower demand for external energy in the CCS process, the land-based cultivation process for algae or the algae-based biofuel processes?

Q2. How do the excess heat levels, in combination with the temperature dependence of the stripper reboiler temperature, affect the maximum CO_2 recovery rates for the MEA and ammonia processes?

Q3. How much heat can be extracted for practical and economical reasons?

Q4. What technical and CO_2 balance advantages does an algae-based biofuel concept exert when integrated with an oil refinery?

Q5. What are the pros and cons of the different techniques for processing algae-based biofuels, for microalgal feedstock and macroalgal feedstock.

1.6 Papers

The thesis is based on the five appended papers. Figure 2 presents a general overview of the contents of these papers and their inter-relationships.

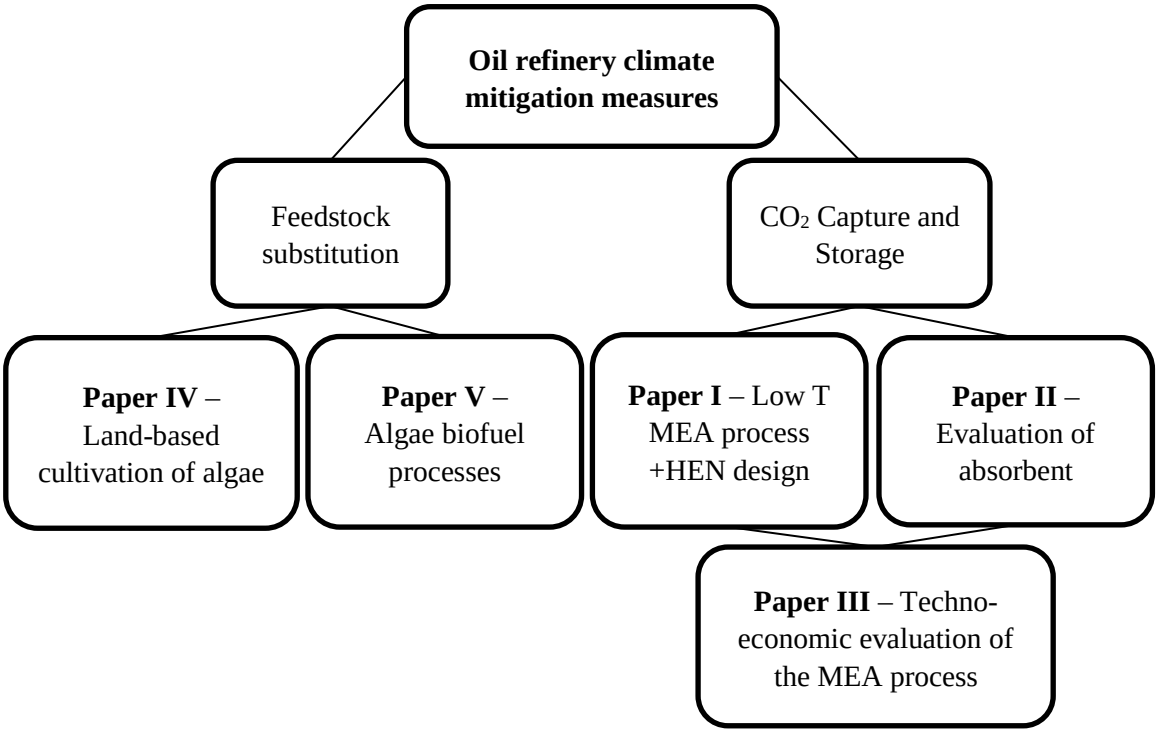

Figure 2: The inter-relationships between the five papers included in this thesis.

Paper I initially describes how the heat of desorption changes with decreasing temperature in the stripper reboiler for the monoethanol amine (MEA) process. This is followed by the construction of three heat exchanger networks (HEN) of different size, and a comparison of the levels of extractable heat from these networks.

Paper II consists of a comparison of the absorbents MEA and ammonia (NH_3), with dependence on generic amounts of excess heat. **Paper II** ends with a case study that investigates which absorbent is most suitable based on maximum CO_2 capture using only excess heat.

Paper III comprises a techno-economical evaluation of the heat exchanger network that was deemed to be the most suitable (in **Paper I**), as well as the absorbent that was found to the best suited to industrial applications (in **Paper II**). The heat exchanger network is evaluated for two levels of amounts, and two concentrations of CO_2 in the flue gas.

Paper IV consists of a comparison of two biorefinery concepts that use land-based cultivated microalgae as feedstock. The evaluated concepts are biodiesel with subsequent biogas production and solely biogas production. A heat balance is constructed across the cultivation pond to decide whether or not a nearby industrial cluster could cover the heat demand.

Paper V describes a process integration study of three biofuel routes that are based on macroalgae and microalgae cultivated at sea. Special emphasis is placed on the material integration aspects.

2 Literature review

This chapter presents the context for this research from the scientific literature.

The literature review (updated per 2015) has been divided into the two main themes for this thesis: CO_2 capture and algae-based biofuels.

2.1 CO_2 capture

As mentioned in the *Introduction*, this thesis is focused on absorption-based post-combustion processes, mainly the MEA process. In **Paper II,** the ammonia process was modelled by Dr. Jilvero. At the beginning of CCS research, the main focus was on how to implement CCS at a power plant in order to be able to continue burning fossil fuels. Subsequently, the research shifted towards a more equal division between CCS for power plants and CCS for industrial applications. This thesis does not deal with the power sector. Nevertheless, the research conducted within the power sector has been important. Even if the conditions are different, the conclusions drawn can be the same. Therefore, only research that is relevant for the process industry is included in the literature review in Section 2.1.1.

2.1.1 General

For the power sector, much effort has been invested in identifying the different operating parameters, in order to decrease the energy demand. Abu-Zahra et al. (2007) carried out a parametric study of the MEA process, investigating lean/rich loadings and the temperature in the stripper reboiler ($T_{Reb.}$), as well as the weight percentage (wt%) of MEA. They concluded that the lowest heat demand was achieved by having temperature of 128°C in the stripper reboiler and using a solution of 40% MEA. However, they cautioned that under these operating conditions, there was an increased risk for heavy corrosion. Notz et al. (2012) conducted an experimental study with temperatures in the range of102°–125°C, and found that one of the most important measures was the minimum temperature difference in the lean/rich heat exchanger.

Alabdulkarem et al. (2012) have used the Aspen HYSYS software to examine how power output could be influenced by better use of waste heat in the CO_2 capture cycle and better integration with the heat recovery steam generator system in an natural gas combined cycle plant (NGCC). They found that an NGCC steam cycle without steam extraction but with a temperature in the condenser that was sufficiently high to supply the stripper reboiler with the necessary heat, provided more electricity than an NGCC with steam extraction cycles.

Ammonia has been discussed as a promising alternative to amines, mainly due to its thermal stability, which is a major problem for alkanolamine-based solvents (EPRI, 2006). The

greatest disadvantage with ammonia is its high vapour pressure, which results in loss of the solvent, in what is termed 'ammonia slip'. In an initial configuration, the absorber was chilled to low temperatures, which allowed precipitation to occur in the solvent and gave low slippage of ammonia. By the end of Year 2012, most studies had shown that chilled ammonia has a heat requirement for regeneration of approximately 2200–2500 kJ/kgCO_2 captured at the standard temperature (Darde et al., 2012; Jilvero et al., 2012; Valenti et al., 2012). However, recent developments have deemed this configuration to be too cumbersome, and a design similar to that of the MEA-based process is currently preferred (Jilvero et al., 2012; McLarnon and Duncan, 2009). Li et al. (2015) performed a study of the parameters of the aqueous ammonia process, in which they varied the stripper reboiler temperature. They showed that the heat of desorption and the sensible heat remained almost constant, regardless of the temperature in the stripper reboiler; it was the heat of vaporisation that changed. The stripper reboiler temperature was varied between 120°C and 165°C, and the specific heat requirement was changed from 4100 kJ/kg to 2800 kJ/kg.

The heuristic rule stated by Gundersen et al. (2009) that both compression and expansion should start at the pinch temperature has been used by Fu and Gundersen (2016) to utilise compression heat as a heat source for three CO_2 capture processes implemented in a coal-fired power plant, none of which were absorption-based. It should be possible to use the heuristic rule also for absorption-based systems, as they have to compress the CO_2 for transport. However, it is not clear how much this would affect the excess heat availability at the expense of a more complicated heat collection system.

2.1.2 Industrial-based and techno-economical studies

Ho et al. (2011) have investigated the costs for CO_2 capture from industrial sources, and have concluded that the cost for capture is higher in refineries than in coal-fired power plants. In a later paper, they compared the costs for an MEA-based system and a Vacuum Pressure Swing Adsorption-based system, at an iron and steel mill, and concluded that the costs for capture would be reduced be 25%–40% if the latter system was used (Ho et al., 2013). However, neither study included excess heat utilisation in the calculations, although they point out that utilising this heat could lead to a lower cost for capture (Ho et al., 2011).

Kuramochi et al. (2012) have concluded that post-combustion CO_2 capture is the only viable option for the cement and oil refinery sectors in the short term, whereas the steel sector has other options. Berghout et al. (2013) investigated the cost of CCS at five different plants, including two oil refineries. They concluded that the most promising and inexpensive technology in a long-term perspective is oxyfuel based on rapid development of the air separation technology that is used. In their calculations for post-combustion at a refinery, they concluded that approximately 60% of the total cost can be attributed to energy, mainly used in supplying heat to the stripper reboiler. In a later study, Berghout et al. (2015) performed a combined techno-economical and spatial footprint study at an industrial park with 16 companies of varying size. They concluded that for absorption-based systems, it was economically favourable to have a semi-centralised absorption system with 10 absorbers spread over the industrial park and a centralised desorption system that consisted of two strippers, with one located at each end of the industrial park. Also here, the economic results were in favour of using oxyfuel combustion, although the CO_2 capture rate was lower.

Jilvero et al. (2014a) performed a techno-economical study at an aluminium plant in which they showed that ammonia is cheaper when the CO_2 concentration approaches 10% in the flue gas, whereas MEA is cheaper when the CO_2 concentration in the flue gas is 3–4%.

Table 1 presents a summary of the techno-economical results previously reported in the literature. The costs reported are avoidance costs (see Section 4.4) at an oil refinery, unless noted otherwise. The reason behind this is that it is difficult enough to compare one oil refinery with another, let alone between different industrial sectors. In Table 1 in **Paper III**, these studies are presented in greater depth, with assumptions made regarding plant life-time and discount rate.

Table 1: CO_2 avoidance costs reported in the literature.
The number in brackets is US$.

Reference	**Technology**	**Emissions from electricity generation (kg_{CO2}/MWh)**	**CO_2 avoidance cost (€)**
van Straelen et al. (2010)	MEA	N/A	30–125
Ho et al. (2011)	MEA	45	63 (87)
Kuramochi et al. (2012)	MEA (short-term)	320–480	66–131
Berghout et al. (2013)	Oxyfuel (short-term)	224–416	49–95
Berghout et al. (2013)	Oxyfuel (long-term)	23–44	22–35
Berghout et al. (2013)	MEA (short-term)	224–416	60–95
Berghout et al. (2013)	MEA (long-term)	23–44	55–84
Johansson et al. (2013)	MEA	0	43–132
Berghout et al. (2015)[1]	MEA	58–396	49–97
Berghout et al. (2015)[1]	Oxyfuel	N/A	36-94

2.1.3 System studies

Hektor and Berntsson (2007) and Johansson et al. (2012) have studied heat integration of post-combustion capture at a pulp and paper mill and at an oil refinery, respectively. Both studies used pinch analysis to elucidate how the demand for heat could be met at the standard solvent regeneration temperature. Process integration was, in these studies, carried out for whole systems. Johansson et al. (2012) have shown that in the oil refinery sector, excess heat alone is not sufficient for meeting the demand for heat in the MEA process, and that heat pumps are beneficial for supplying external heat.

Rootzén and Johnsson (2013) performed an analysis of the European oil refinery sector, cement industry, and iron and steel industry. They concluded that for none of the sectors investigated was it possible to achieve the reductions needed up to Year 2050 using existing production processes. They emphasised that efforts to develop new low-carbon production processes must increase and suggested that if a breakthrough in this area does not emerge

[1]These studies were made at an industrial park that comprised one refinery and 15 other plants. The results are not presented in Table 1 of **Paper III**, as they were not published at the time of submission.

soon the industrial sector will not reach the target of reducing CO_2 emissions by 95%. In a subsequent study, they discussed the possibility of industry-based CCS for the same sectors but now focused on the Nordic countries; they established that there are several problems associated with (for example) the geographical spread of the emissions, which presents an obstacle to an efficient transportation and storage network (Rootzén and Johnsson, 2015).

Zhao et al. (2015) proposed a system that involves solar-assisted post-combustion CO_2 capture in China. They concluded that this system was feasible and would lead to a reduction in the carbon intensity of CO_2 capture processes, the magnitude of the reduction being dependent upon the size of the solar field.

2.2 Algae-based Biofuels

2.2.1 Biofuel processes

As mentioned in Section 1.4, various biofuels have been derived from algae. The most common ones are described below.

Biodiesel production (lipid extraction)

The benchmark process is biodiesel production through lipid extraction. This is usually carried out with microalgae, as macroalgae do not contain high levels of lipids (Alaswad et al., 2015). The process involves the following steps: pre-treatment; extraction; and transesterification (Pokoo-Aikins et al., 2009). Lee et al. (2010) tested different pre-treatment protocols and concluded that microwave irradiation with simultaneous heating was a simple yet effective way of disrupting the cell walls. Methods to extract the lipids from the algae include *in situ* and conventional extraction techniques (Ehimen et al., 2009). Li et al. (2014) produced a list of the benefits and drawbacks of each method, and concluded that the loss of lipids was lower in the conventional lipid extraction process. Recent results suggest that that CO_2-expanded methanol gives a higher yield from lipid extraction than the traditional organic solvent extraction (Yang et al., 2015). Transesterification into FAME is a standard process, and is described in Section 3.2.2.

Renewable diesel (hydrothermal liquefaction)

A route to biofuels that has drawn increasing interest in recent years is hydrothermal liquefaction (HTL). This thermochemical process produces (at high temperatures and pressures) a so-called 'biocrude' oil (Elliott, 2007). Biller and Ross (2011) investigated the yields of oil from HTL with different biochemical compositions. They found that lipids gave the highest yield of biocrude, followed by protein, and the lowest yield was from carbohydrates. Carbohydrates are the only components that benefit from the inclusion of a catalyst in the process. Many papers have described the yields and compositions of different algae strains, mostly microalgae (Li et al., 2014; Valdez et al., 2012; Zhang et al., 2013) but also macroalgae (Anastasakis and Ross, 2015; Bach et al., 2014). Valdez et al. (2014) developed a kinetic model to predict the yields of biocrude, aqueous phase, gas, and solids as a function of the initial composition of the microalgae. Rate constants were produced for four different temperatures with a reasonably good fit. Roberts et al. (2012) made a comparison of the biocrude yields from macroalgae and microalgae (grown under the same conditions) and found that on a dry ash-free weight basis, the yields of biocrude were

similar, both in terms of energy density and elemental composition with respect to carbon, hydrogen, and oxygen.

Biogas

Since the 1950s, algae have been used to produce biogas through anaerobic digestion (Golueke et al., 1957). It is basically the same process that is used today, although improvements are on the way. Xia et al. (2016) suggested three scenarios based on the maturity of the technology. They claimed a three-fold increase in the theoretical yield when they changed from today´s technology to a more advanced technology, and a two-fold increase when they changed to a technology that is forecasted to be commercially available in a few years.

Both the lipid extraction route and the HTL route from biomass to biofuel leave a significant amount of organic material as residue (Frank et al., 2012; Pokoo-Aikins et al., 2009). The organic material can be subsequently converted into biogas.

Ethanol production

Algae contain high levels of starch that can easily be converted to bioethanol (John et al., 2011). Hirano et al. (1997) investigated the impact of dark, anaerobic digestion on the energy efficiency of the starch-to-ethanol process. They concluded that the algae started to produce not only starch, but also ethanol when the algal biomass was exposed to these conditions. Martín and Grossmann (2014) developed a pathway to use glycerol, which is a by-product of biodiesel production, for bioethanol production. They found that when extracting the lipids for biodiesel production and employing the algal residues for bioethanol production, the use of glycerol for fermentation increased the yield of bioethanol by almost 50%.

Gasification

Algae gasification has mostly been investigated as a complement fuel with a mix of, for example, 10% algae and 90% coal (Zhu et al., 2015). That is due to the high ash content of algal biomass, which raises an operational risk for gasification, such as bed sintering or agglomeration, as reported elsewhere in the literature (Alghurabie et al., 2013; Yang et al., 2013). It could prove useful to co-gasify algal pellets with other types of biomass. However, in this thesis, the focus is on routes in which algae are the only feedstock.

2.2.2 Marine-based cultivation of algae

Marine-based cultivation relates particularly to macroalgae, although some attempts have been made to apply marine-based cultivation also to microalgae. There are many differences between the systems. For microalgae, marine-based cultivation assumes the use of closed systems (since their size makes them difficult to harvest), often called ‘photobioreactors’, such as plastic bags or more advanced systems (Bharathiraja et al., 2015; Verhein, 2015). In contrast, the cultivation of macroalgae is most commonly achieved by cultivation on a rope (Aitken et al., 2014; Chen et al., 2015; Peteiro et al., 2014). While macroalgae can use the nutrients that are present naturally in the water, microalgae must be fed a growth medium that contains all the necessary nutrients (Bharathiraja et al., 2015).

2.2.3 Land-based cultivation of algae

The land-based system mostly concerns the microalgae. Algae can be grown in open or closed systems. Open systems, such as lakes and ponds, can more easily be used for scaling up production, since they are less technically complex than closed systems (Jorquera et al., 2010). The cultivation system should be designed so that solar radiation reaches all the algal cells in an efficient manner. Despite the high production capacity of open ponds, water temperature, vapour losses, CO_2 diffusion to the atmosphere, and the risk of contamination result in lower productivity levels than can be achieved using closed systems (Demirbas, 2010). Photobioreactors offer a regulated and controlled cultivation environment and reduced risk of contamination. A large surface area in the bioreactor also increases the amount of light that reaches the algae. In a photobioreactor, the efficiency of CO_2 fixation is higher than in an open system due to superior mixing possibilities (Ho et al., 2011). In addition, thermal insulation is enhanced in closed systems compared to open systems, although the scaling up of closed systems has other drawbacks, e.g., they are more expensive than open ponds and there exist limitations as to their size (Demirbas, 2010).

2.2.4 Microalgae cultivation in wastewater

There are numerous studies that demonstrate that microalgae can thrive in municipal wastewater (Aziz and Ng, 1992; McGriff Jr. and McKinney, 1972; Tam and Wong, 1989). The algae can also remove heavy metals, pathogens, and other contaminants from wastewater (Rawat et al., 2010; Wang et al., 2009). Life cycle assessment (LCA) studies show that around 50% of the CO_2 emissions originate from the production of nutrients (Clarens et al., 2010). Therefore, it is of importance for the energy and CO_2 balances that these nutrients are not produced artificially.

Since municipal wastewater shows a deficit of carbon for optimal nitrogen removal (Craggs et al., 2011; Park et al., 2011), it can be advantageous to bubble industrial flue gases through the cultivation pond (Craggs et al., 2011).

2.2.5 System studies and life cycle assessments

Energy analyses of the different biofuel routes are available, although these analyses generally do not take into account the possibility of using industrial excess heat as a heat source.

Pokoo-Aikins et al. (2009) performed a pinch analysis of the lipid extraction process. Using a previously reported cultivation process to grow the algal strain *Chlorella*, with 30% or 50% lipid content, and they heat integrated the whole process to find the minimum heat demand. They found that heat integration was beneficial and decreased the payback period. They did not, however, consider co-location with an industrial plant.

Zhang et al. (2014) compared anaerobic digestion and HTL as measures for energy output and nutrient recovery for use in algal cultivation after first extracting the lipids from the microalgae. They concluded that while more nitrogen was recovered in the anaerobic digestion process, HTL gave a higher recovery rate of phosphorus. They also concluded that the HTL process yielded a higher rate of energy recovery, despite the fact that before entering the HTL process the lipids were extracted from the biomass. In the earlier study mentioned above, Biller and Ross (2011) concluded that, in the HTL process, lipids yielded

the highest conversion from biomass to biocrude. Similar findings to those reported by Zhang et al. (2014) were made by Venteris et al. (2014), who compared microalgae-based HTL and lipid extraction. They found that the nitrogen demand increased when performing HTL but that the phosphorus demand decreased. Venteris et al. (2014) also found that the demand for water clearly decreased with the HTL route.

Life cycle assessments (LCA) of both microalgae- and macroalgae-based biofuels have also been carried out (Aitken et al., 2014; Alvarado-Morales et al., 2013; Connelly et al., 2015; Frank et al., 2012). Aitken et al. (2014) performed an LCA of macroalgae-derived biogas, alternatively ethanol production, or ethanol production with subsequent biogas production. They found that none of these routes was sustainable according to the sustainability metrics of Hall et al. (2009) (an energy return on investment of 3), although ethanol production without subsequent biogas production came close with an energy return on investment of 2.95. Alvarado-Morales et al. (2013) investigated two brown macroalgae that are commonly found off the coast of Denmark from an energy perspective, as well as from a greenhouse gas emissions perspective for ethanol with subsequent biogas production or biogas production. They concluded that biogas production performed better than bioethanol production with subsequent biogas production for all the categories investigated.

Posada et al. (2016) investigated 10 microalgae configurations for lipid extraction processes, comparing both non-energy and energy end-products. They concluded that the non-energy products were the most efficient in the form of greenhouse gas emissions, and that further conversion to biodiesel or green diesel was not desirable. They also found that the worst economic performance was associated with the configuration in which the oil-free residues were digested further to biogas.

Frank et al. (2012) explored the energy balance between the lipid extraction of microalgae process and microalgae-based HTL and found that more efficient utilisation of whole algae biomass makes the HTL route more material-efficient. However, electricity and heat generation *via* the HTL route was not sufficient to cover fully the energy demand of algal cultivation, given that the biocrude yields were more than 40%. In their analysis, more nitrogen was present in the HTL oil than in the lipid slurry, which could be a problem, given that the nutrients were produced artificially and not recycled.

2.3 Other CO_2-mitigating options for oil refineries

2.3.1 Energy efficiency

According to Brown (1999), more than 35 refineries have performed total site analyses in the period 1992–1999. Energy efficiency was not necessarily the primary motivation in these evaluations (capital cost reductions for future expansions, and debottlenecking can be mentioned among the benefits), although still the average energy savings was 20%–25%. When taking economy into account, energy savings of 10%–15%are typically achievable.

E. Andersson et al. (2013) conducted a heat integration study at a complex refinery, and concluded that the theoretical savings potential in terms of heat were 50%, without taking into consideration distance or other practical issues. The result changed to an approximately

30% reduction in heat demand when the proximity of the process streams to each other was considered. A further decrease in the potential (to 6%) occurred when streams that were already cooled in the utility were utilised in the five largest areas to generate medium-pressure steam. No economic calculations were performed in that study.

Morrow et al. (2015) made an estimate of energy efficiency for the US oil refining industry, through the development of a notional refinery model, while cautioning that no two refineries are identical. They considered actions as diverse as reactor improvements to information management, and concluded that while a less-energy-conscious industrial sector (cement, and iron and steel were mentioned) had more low-hanging fruits available, the US oil refining industry could implement 35 Mt_{CO2}/y in cost-effective savings. An additional 50 Mt_{CO2}/y could potentially be cost-effective, while other measures were technically feasible but not cost-effective. The total CO_2 emissions of the US oil refining industry amount to 178 Mt/y (EPA Facility Level GHG Emissions Data, 2016)

2.3.2 Low-carbon energy sources

One way to use low-carbon energy is through electrification of the industry (Jacobson et al., 2014). The electricity grid would then have to be based primarily on renewable energy, such as wind-, solar-, and water-based generation. Jacobson and Delucchi (2011) have proposed a roadmap in which the entire global energy system is based on renewable energy. In their study, they do not consider nuclear power and CCS to be sustainable in the long-term perspective, and they do not consider biomass combustion. Jacobson and Delucchi (2011) have concluded that such a system would reduce the world electricity demand by 30% in Year 2030, primarily due to the efficiency gain from switching from internal combustion to electricity.

Hertwich et al. (2015) performed an LCA in which they compared the IEA Blue Map scenario to the Baseline scenario. Biofuels were excluded from this analysis. They concluded that compared with Year 2010, the Blue Map scenario would lead to a substantial reduction in CO_2 emissions while doubling the output of electricity. Meanwhile, a doubling of all pollution-related indicators was the result of implementing the Baseline scenario. Only a moderate increase in the material requirement was observed when implementing the Blue Map scenario, and the supply of copper was the only concern with regard to the materials integrated in the analysis.

Although systems such as those presented above would ultimately render oil refineries obsolete (if they included electrification of the transportation sector), refineries are not predicted to disappear anytime soon (CONCAWE, 2013).

Another option to decrease emissions is the use of hydrogen for combustion purposes (Jacobson et al., 2014). Although steam reforming of methane for hydrogen production is encumbered with CO_2 emissions, with an electricity system such as that discussed above the hydrogen could be produced *via* electrolysis. The hydrogen could also be produced *via* the gasification of wood (Brau and Morandin, 2014), steam reforming of ethanol (Haryanto et al., 2005), or using algae (Berlin et al., 2013).

3 Studied systems

This chapter describes the systems that are studied in the different papers.

3.1 CO_2 capture

While several post-combustion CO_2 capture techniques exist, the one that is most commonly employed is chemical absorption using amines. Various amines, such as MEA, ammonia, piperazine, and methyl diethanolamine (MDEA), can be used in the process. In this work, the most intensively investigated option for chemical absorption of CO_2 is MEA, given that is the most highly developed system and has been used in the gas cleaning industry for several decades. In **Paper II,** the ammonia process was modelled by Dr. Henrik Jilvero in co-operation with the author of this thesis. The ammonia process was modelled in direct comparison with the MEA process.

The CO_2 capture process is outlined in Figure 3, where the units enclosed in boxes with dashed lines are present exclusively in the ammonia process. Regarding the design and configuration, the loading has been kept constant (see Section 4.5). The CO_2 capture processes are heat-integrated, which means that only the resulting heat demand after heat integration is shown. In the generic amine process, the flue gas first enters the absorption column (A1), where it is bubbled through the CO_2-lean absorption fluid. As the flue gas ascends the column, the CO_2 dissolves in the absorption fluid; by the time the flue gas exits the top of the column it has lost 85% of the CO_2 that it originally contained. The CO_2-rich absorption fluid thereafter proceeds through a pre-heater on to a stripping column (S1), where heat is added and the solubility of CO_2 in the absorption fluid decreases, causing the CO_2 to be released. The CO_2 is subsequently compressed and dried, to attain the required pressure and purity. In the case of ammonia, some of the absorption fluid follows the flue gas out of the absorber, necessitating a second absorption/stripping cycle, called the abatement cycle (A3/S2).

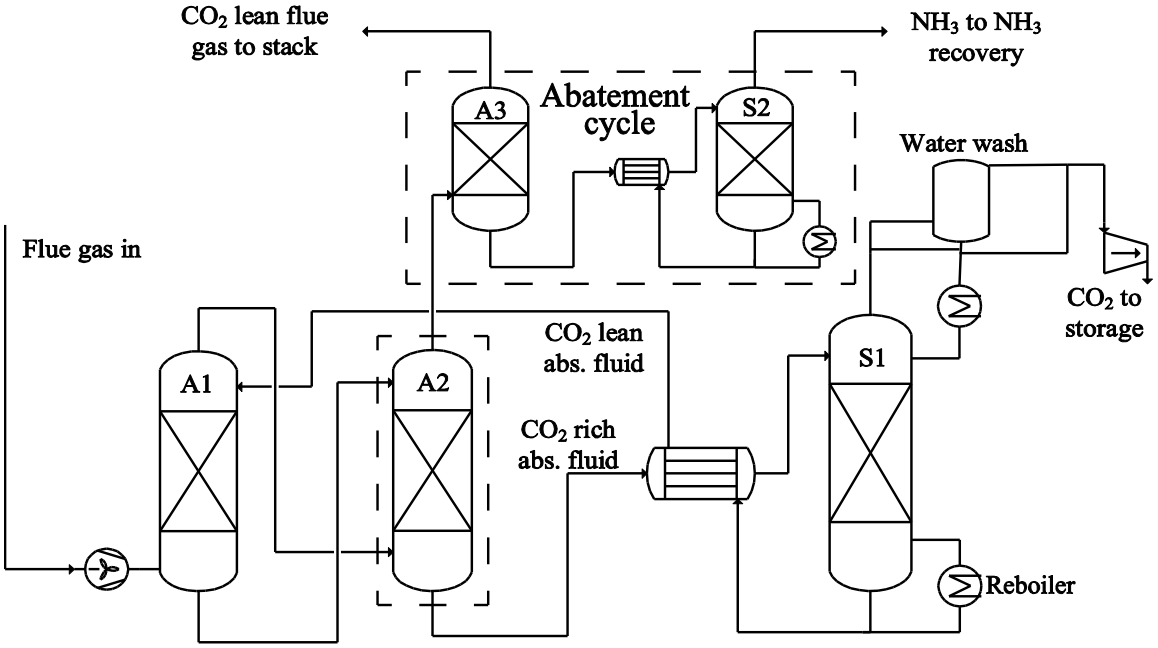

Figure 3: General set-up for a post-combustion CO_2 capture process as modelled in this work. The units enclosed in boxes with dashed lines exist exclusively in the ammonia process.

3.1.1 Generic quality and amounts of heat

The quality and amount of excess heat available are factors that must be considered when choosing the solvent and the stripper reboiler temperature for a heat-integrated, absorption-based CO_2 capture process in an industrial application. The excess heat is best represented by an Actual Cooling Load Curve (ACLC, see Section 4.1). An investigation was made to determine how the CO_2 capture rate changes with decreasing temperature, starting at the standard temperatures of 120°C for MEA and 155°C for ammonia. The temperature intervals chosen were: 90°–120°C plus a ΔT_{system} value of 10 K for MEA; and 105°–155°C plus a ΔT_{system} value of 10 K for ammonia. For a definition of the ΔT_{system} term, see **Paper I**. In these theoretical cases, the ACLCs are all assumed to be linear within the temperature interval. This investigation was performed through an analysis of the ratio of the additional excess heat available in the given interval to the total heat available until the lower temperature limit of the interval (Q_{add}/Q_{tot}) is reached (see Figure 4). For a given Q_{add}/Q_{tot} ratio, it is only the derivative in the temperature interval (which is assumed to be linear as a first approximation) that matters. The appearance of the ACLC at either side of the temperature interval (illustrated by the dashed lines in Figure 4) is of no consequence, as it is only the amount of excess heat that is important.

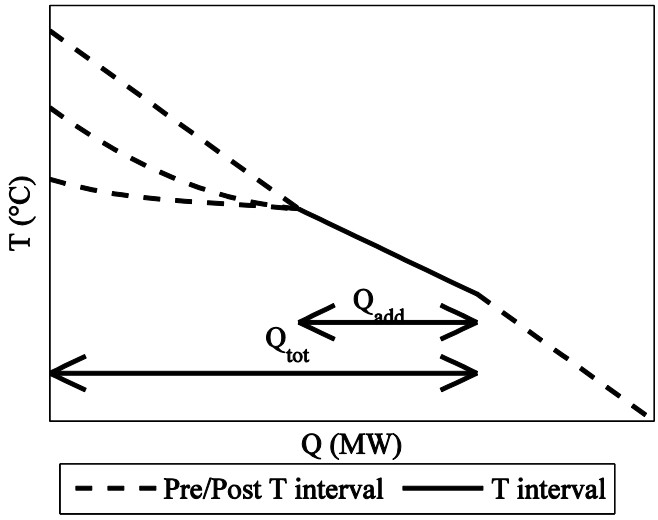

Figure 4: Depiction of the Q_{add}/Q_{tot} ratio.

3.1.2 Case study complex oil refinery

The case study oil refinery presented in **Papers I-III** and **V** is a complex refinery located on the west coast of Sweden that emits around 1.8 Mt CO_2/y. The majority of the emissions is from the four main chimneys, which are those deemed feasible for CO_2 capture or utilisation throughout this work (Grönkvist, 2010). A CO_2 capture or biofuel production plant could be added to the refinery at the southwest corner (within the box with dashed lines in Figure 5).

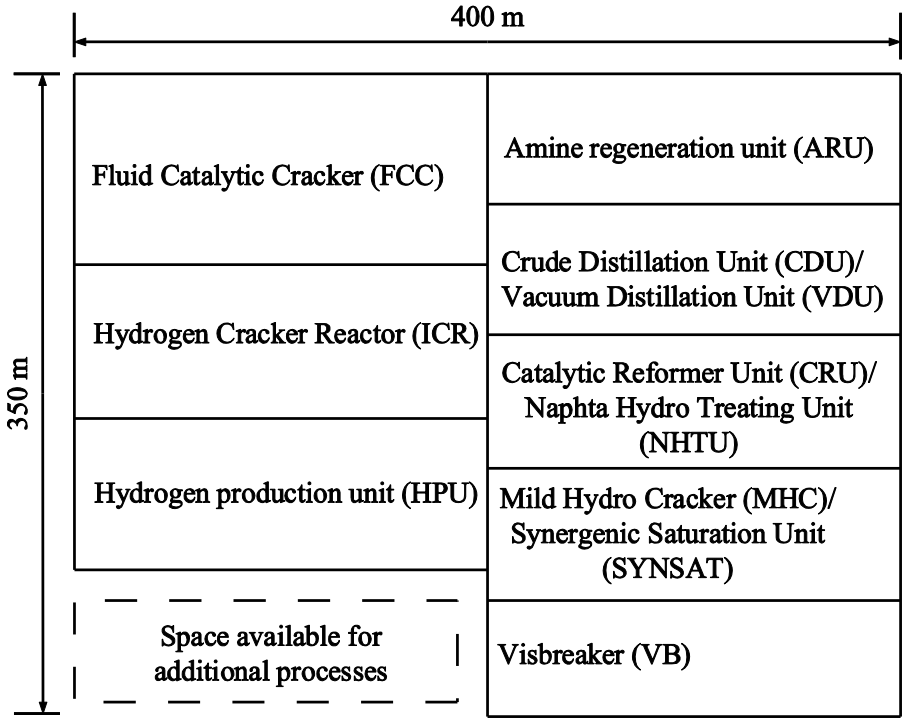

Figure 5: Overview of the case study refinery presented in **Papers I-III** and **V**.

Heat integration possibilities

As part of a project conducted by E. Andersson et al. (2013), the heat flows of the refinery have been mapped. The subsequent pinch analysis at the refinery reveals the possibilities for excess heat utilization and is the basis for **Papers I-III** and **V**. The heat mapping was carried out on all 13 different areas of the site; in addition to studying individual heat flow characteristics, an aggregate analysis was also performed. In Figure 6, some of the outcomes of the aggregate analysis are shown. Figure 6a shows the case in which a theoretical heat exchanger network for maximum heat recovery is installed, thus obviating the need for both heating below the pinch and for cooling above the pinch, which occurs at approximately 130°C. Figure 6b shows the utility cooling at the refinery. As expected, there is cooling also above the pinch. Operational security and other concerns entail that units are not connected through heat exchangers and cooling takes place above the pinch. Energy efficiency measures may reduce to some extent the difference between the curves depicted in Figure 6a and Figure 6b. However, E. Andersson et al. (2013) estimated that of the identified 210 MW of energy efficiency measures, about 20% was economically feasible. The cooling utility system consists of more than 100 heat exchangers. **Paper I** looks at how to decrease the number of heat exchangers without significantly reducing the amount of heat that is extracted.

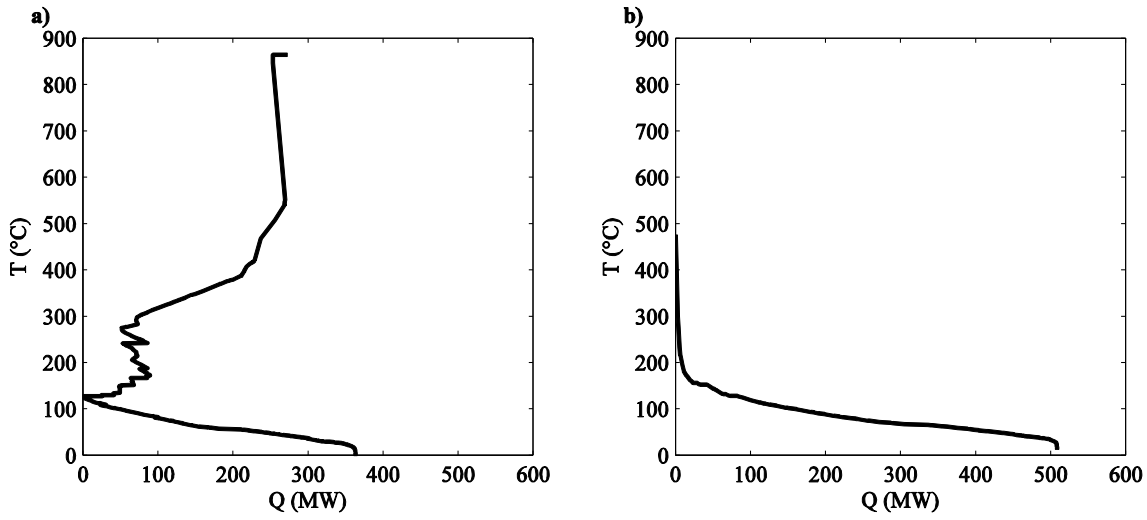

Figure 6: Heat flows at the refinery. a) A situation in which the heat is optimally heat-exchanged. b) A case that show all heat that currently is cooled away by utility.

3.2 Algae-based biofuel

3.2.1 Algae-based biofuel processes

As with any biomass, there are several pathways to produce a fuel. When choosing pathway, the most important considerations are the material and energy efficiencies of the different routes. To maximize these two efficiencies, all the biofuel production routes investigated in this thesis are end with either catalytic hydrothermal gasification (CHG) or

anaerobic digestion, so as to utilise any organic content that remains in the feedstock. The most important data regarding algae-based biofuel production are shown in Table 2.

Table 2: Algae-based biofuel production.

Material	HHV		Reference
Nannachloropsis (microalgae)	16.8	MJ/kg db	(Sukarni et al., 2014)
Saccharina latissima (macroalgae)	12.2	MJ/kg db	(Anastasakis and Ross, 2015)
Biodiesel (R1)	37.8	MJ/kg	(Pokoo-Aikins et al., 2009)
Renewable diesel (R2)	34.5	MJ/kg	(Biller and Ross, 2011)
Renewable diesel (R3)	33.2	MJ/kg	(Anastasakis and Ross, 2015)
Biochar (R3)	17.2	MJ/kg	(Anastasakis and Ross, 2015)
Biogas	39.3	MJ/m^3	(E. A. Ehimen et al., 2009)

The rationale for choosing these particular strains of algae is that they are among the most intensively studied, so reliable data can be obtained. In the case of the microalgae, tolerance to variations in salinity has also been a factor. The present study was performed with the aim of identifying the parameters that are important and that can be coupled to further studies.

The studied routes are:

R1. Biodiesel production from microalgae *via* lipid extraction and transesterification. Subsequent anaerobic digestion, to convert the remaining carbon into biogas, is also modelled.

R2. HTL with a microalgal feedstock. CHG is used to convert the organic carbon remaining in the aqueous phase after HTL. The products are a biocrude, which is similar to regular crude oil, and biogas.

R3. HTL with a macroalgal feedstock. CHG is used to convert the organic carbon remaining in the aqueous phase after HTL. The products are a biocrude (similar to regular crude oil), biogas, and biochar.

Both algal types have to be dried to 20 wt% dry matter before entering the processes.

3.2.2 Biodiesel production with subsequent biogas production (R1)

For all the basic data regarding R1, see **Paper IV** and Andersson et al. (2011). The system has been updated with the new compositions of the microalgae (Biller and Ross, 2011), and the anaerobic digestion of wastewater sludge has been removed.

The algal slurry is first dried in several stages (to 20 wt% dry matter) and is pre-treated in a stirred ball-mill before it enters the lipid extraction process, where butanol is used as the extraction fluid. Upon the removal of butanol, the lipids are transesterified using methanol at a molar ratio of 6:1 (Pokoo-Aikins et al., 2009). After the transesterification reaction, the byproduct glycerol constitutes 10% of the ingoing reactants and is assumed to go to biogas production, as do the residues of the lipid-extracted algae. The biodiesel process with subsequent biogas production is depicted in Figure 7.

The values for the heat demands are taken from Pokoo-Aikins et al. (2009).

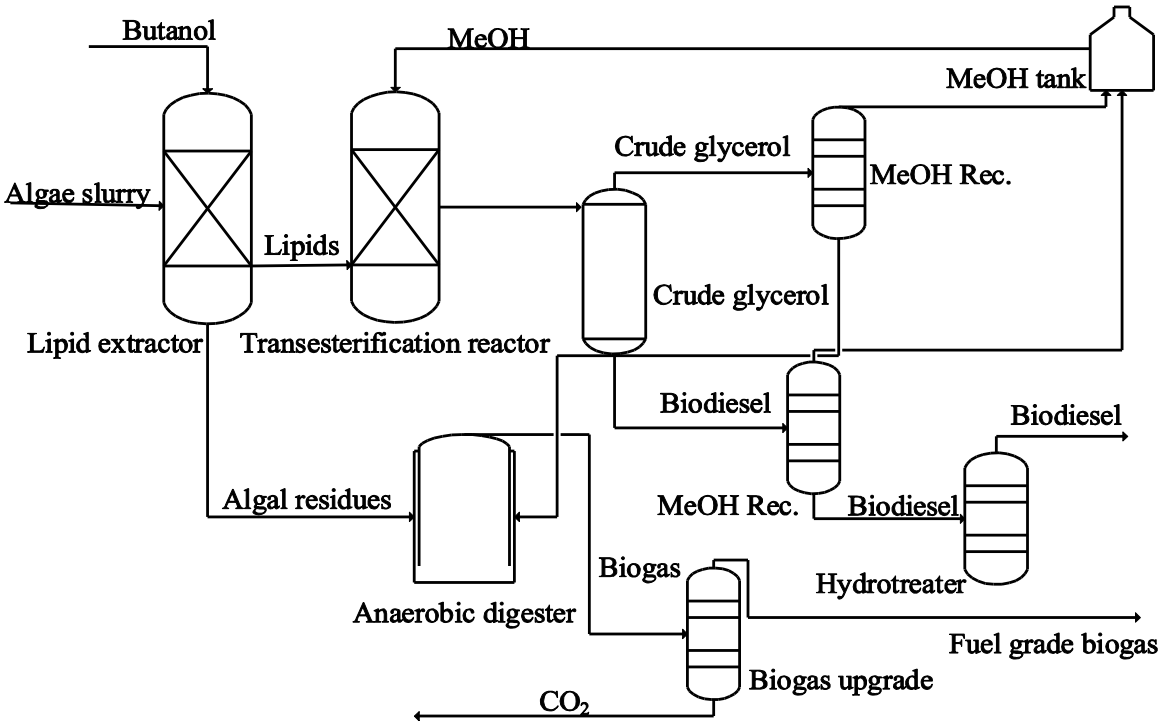

Figure 7: The biodiesel with subsequent biogas process modelled in this work.

Paper IV uses the Redfield standard algae composition $C_{106}H_{181}O_{45}N_{15}P$ (Davis et al., 2011) and **Paper V** uses the algae *Nannochloropsis* (Biller and Ross, 2011).

3.2.3 Hydrothermal liquefaction with subsequent catalytic hydrothermal gasification (R2, R3)

For all the basic data regarding R2 and R3, the reader is referred to **Paper V**. The HTL system is modelled in two different ways, depending on whether the feedstock is microalgae or macroalgae. However, the process outline is the same [based on the work of Frank et al. (2012), which was further developed by Jones et al. (2014)] and is shown in Figure 8. The microalgal strain used is *Nannochloropsis* and the macroalgal strain used is *Saccharina latissima*.

The yields of the different products are taken from Biller et al. (2015) and Biller and Ross (2011) for the macroalgal system. For the microalgal system, the process kinetics described by Valdez et al. (2014) are used in conjunction with the same algae composition as in R1 (Biller and Ross, 2011), to determine the product output.

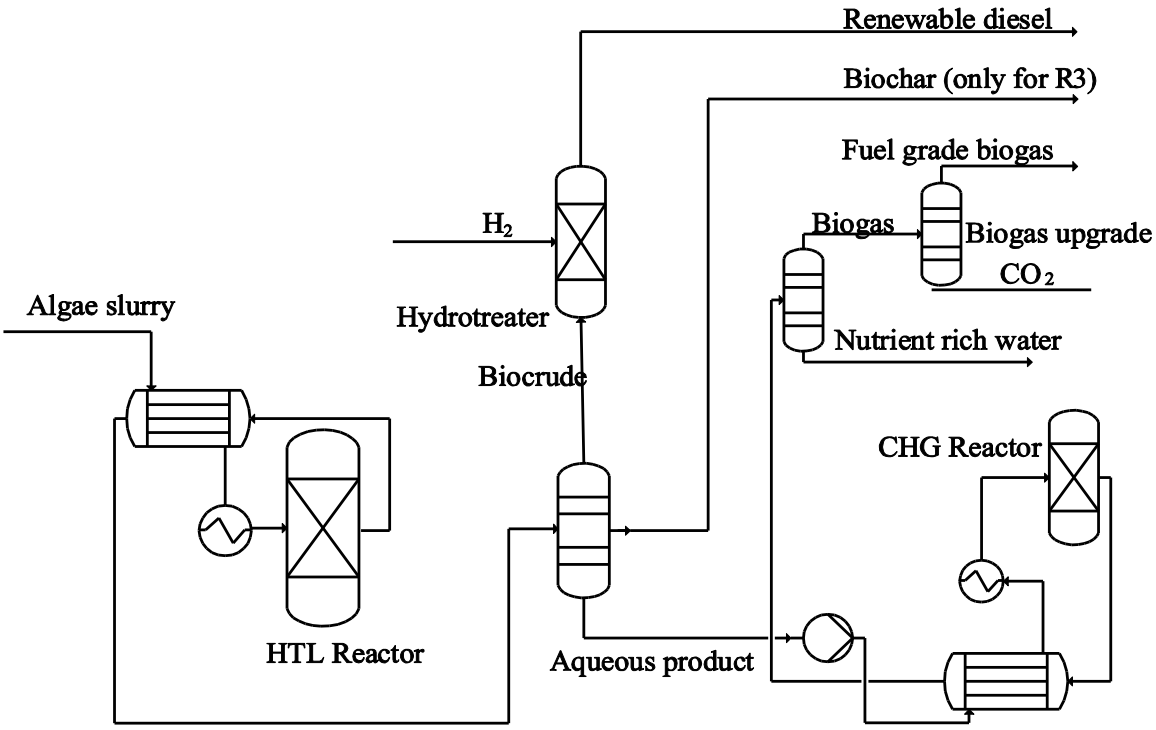

Figure 8: Outline of the HTL process modelled in this work.

3.2.4 Industrial cluster at Hisingen

Paper IV describes the integration of an algae-based biofuel concept with an industrial cluster at Hisingen, Gothenburg, Sweden. The cluster consists of two oil refineries (Preemraff Göteborg and ST1), one NGCC (Ryaverket) plant, and one wastewater treatment plant (Gryaab). Having different plants in proximity to one another is the basic idea behind industrial clusters, where one or more plants can draw benefits from process integration aspects of the other plants in the cluster.

An overview of the industrial cluster is presented in Figure 9.

Heat integration possibilities within the industrial cluster

The industrial plants produce high levels of excess heat, along with flue gases that contain CO_2. In this study, it was assumed that only excess heat at <90°C could be used to heat the algae cultivation pond, as excess heat with temperatures >90°C would be used in the district heating system of Gothenburg. One of the two refineries has approximately 105 MW of heat, which is currently cooled by utility to <90°C (Andersson et al., 2014a). It was assumed that since the second refinery has two-thirds of the crude oil capacity of the first refinery, 70 MW of heat is available at this facility, yielding a total of 175 MW of heat for heating the algae cultivation pond.

Material integration possibilities within the industrial cluster

Nutrients from the wastewater can be used to meet the demands of algae cultivation. The cultivation is designed to be able to treat the entire flow of wastewater from the city of Gothenburg. CO_2-rich flue gases from the refineries, as well as from the NGCC plant, could

be used to compensate for the carbon shortage that results from algae being cultivated in wastewater (Craggs et al., 2011). By co-locating the algae cultivation and the WWTP, the majority of the wastewater treatment could be replaced by the cultivation site (see Section 2.2.4), and this could then be regarded as an environmental benefit of the system (Craggs et al., 2011; Park et al., 2011).

The NGCC can receive the produced biogas, and when the NGCC is not operating, the refineries can use the biogas in their processes. The refineries can also use the liquid fuels produced as a drop-in fuel in their fossil-based diesel, or use their existing infrastructure to distribute the produced biofuel.

All these options are considered in **Paper IV**.

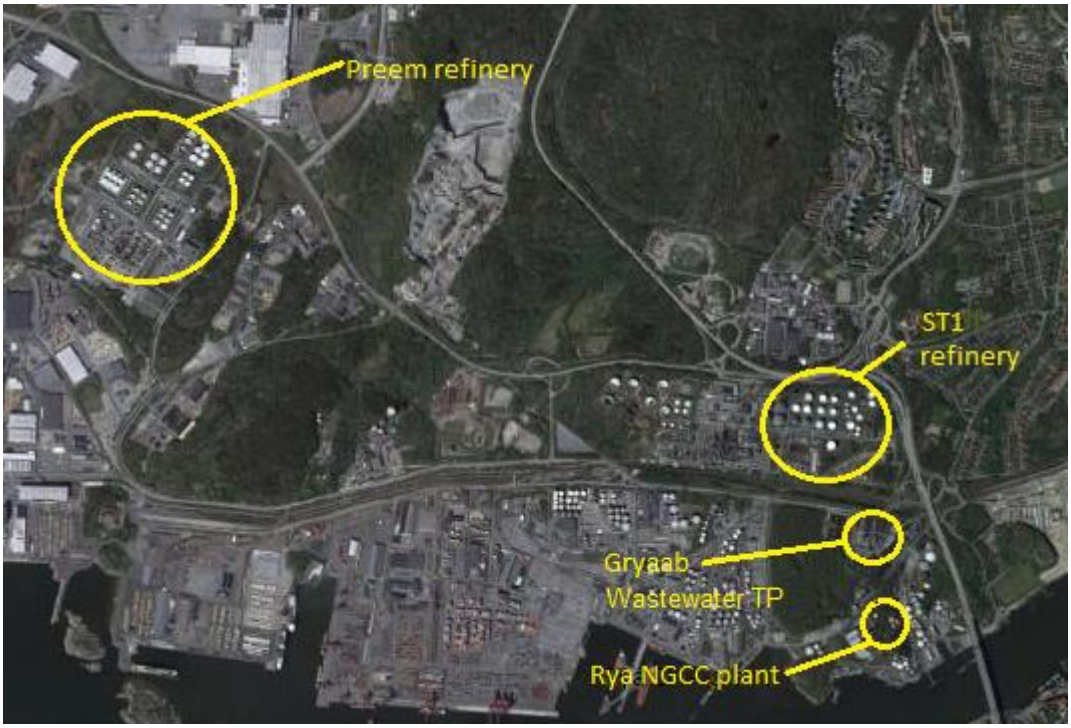

Figure 9: The industrial cluster at Hisingen, which includes two refineries, one wastewater treatment plant, and an NGCC plant. © Lantmäteriet Gävle. Medgivande I 2011/0072.

3.2.5 The complex oil refinery

The complex oil refinery system is identical to the heat integration unit described in Section 3.1.2. For the algae-based biofuel, material integration in addition to heat integration plays an important part.

Material integration possibilities at the complex oil refinery

The refinery has a steam reformer that reforms methane to produce hydrogen. This hydrogen can be used to satisfy the hydrogen demand of the biofuel upgrading process. In return, all the algae-based biofuel routes investigated produce biogas that can be used to feed the steam reformer. The refinery can also use the liquid fuels produced as drop-in fuels

in their fossil-based diesel, or use their existing infrastructure to distribute the produced biofuel.

All three routes have been modelled individually (in **Paper V**), both as a stand-alone plant and an integrated plant. A stand-alone plant has neither the heat integration possibilities nor the material integration possibilities described above. The hydrogen production technology assumed for stand-alone plants is electrolysis, given that algae-based biofuels represent a system for the future and electrolysis is the hydrogen production technology linked to future sustainability (Turner, 2004). Since the choice of hydrogen production technology depends heavily on the time perspective used, a sensitivity analysis regarding hydrogen production technology is presented in **Paper V**.

4 Methodology

This chapter describes the different methodologies used in the studies described in the appended papers, and specifies in which studies they are used.

Four different methods for process design and evaluation are presented in this thesis. In Table 3, the methods are paired with the respective research question (see Section 1.5).

Table 3: Methods used for answering the research questions

Research question	**Method(s)**
Q1	4.1 Process integration
	4.2.1 Modelling of CO_2 capture
Q2	4.1 Process integration
	4.2.1 Modelling of CO_2 capture
Q3	4.1 Process integration
	4.4 Techno-economical evaluation
Q4	4.1 Process integration
	4.2.2 Modelling of algae-based biofuel routes
	4.3 CO_2 emissions consequences
Q5	4.1 Process integration
	4.3 CO_2 emissions consequences

4.1 Process integration

All the appended papers use process integration, which is defined by the IEA as "systematic and general methods for designing integrated production systems ranging from individual processes to total sites, with special emphasis on the efficient use of energy and reducing environmental effects" (Gundersen, 2000). **Papers I-III** mainly use heat integration,

although they could also be considered to include mass integration, since CO_2 is an input to the capture unit. **Papers IV** and **V** use a more general approach to process integration, whereby both mass and heat flows are interchanged across different parts of the industrial cluster.

The most frequently used tool in this thesis is pinch analysis. Pinch analysis is a first and second law-based tool that can be used for systematically estimating the theoretical minimum applications of heating and cooling. It has been developed to include a range of utilities other than heat, e.g., water and hydrogen. For a thorough description of the tool, see the studies of Smith (2005) and Klemes et al. (2010).

Throughout this thesis, Actual Cooling Load Curves (ACLC's) are used consistently to define the available excess heat of the oil refinery (Nordman and Berntsson, 2001). The ACLC reflects how much heat is cooled to the ambient temperature by utility (air or water). To describe the biofuel processes in **Paper V** and to describe the CCS processes in **Paper II**, a Grand Composite Curve (GCC) is used. The GCC reveals the heating and cooling demands for a given minimum temperature difference that is allowed in a heat exchanger (ΔT_{min}), assuming that maximum internal heat recovery is implemented.

Background/Foreground curves (BG/FG) show a mirrored GCC for the foreground process (e.g., a CCS plant or an algae-based biofuel plant) in the same figure as an ACLC of the background process (i.e., the oil refinery processes) (Smith, 2005). This allows the sizing of the foreground process based on how much heat there is available in the background process.

In **Papers IV** and **V,** mass integration is considered. In **Paper IV,** an industrial cluster that consists of two oil refineries, one NGCC plant, one wastewater treatment plant (WWTP), and one biofuel production plant is assumed. This creates possibilities for the exchange of both products and waste streams between the different plants in the cluster.

4.2 Modelling

Process modelling constitutes a significant portion of the work presented in this thesis. The models are divided into CO_2 capture processes and algae-based biofuel production processes.

4.2.1 Modelling of CO_2 capture

The main focus of this thesis is on the MEA process. In the co-authored **Paper II,** Dr. Jilvero contributed with modelling of the ammonia process. The author is aware that more advanced absorbents (such as piperazine and MDEA) exist but has limited his study to the more traditional MEA absorbent, given the higher level of knowledge about this absorbent at the start of the work.

Two absorbent-based CO_2 capture processes are described in the papers. The MEA process (**Papers I-III**) and the ammonia process (**Paper II**), both of which have been modelled in the Aspen Plus software, are considered. Modelling of the MEA process is performed using the Aspen Plus KMEA package, which contains kinetic data for the interactions between MEA, water, and CO_2. The absorber uses the kinetic data; however, as the reactions that

take place in the stripper are rapid and as long as the internal profiles of the stripper are not studied, the stripper can be modelled as being in equilibrium with good results (Abu-Zahra, 2009). For the ammonia process, which was modelled as being in equilibrium by Dr. Jilvero, the data are also derived from the standard Aspen Plus package. Both models use the ELECNRTL base method, albeit with different property methods: SYSOP15M for MEA; and PC-SAFT for ammonia. For a thorough description of the models, see V. Andersson et al. (2013) for the MEA model and Jilvero et al. (2012) for the ammonia model.

Both systems have been modelled for various temperatures of the stripper reboiler, in order to investigate the heat integration possibilities for the case study oil refinery. Process parameters have been kept as constant as possible, for instance, the same rich and lean loadings are used for all the modelled temperatures (see Section 4.5). The lean and rich loadings used for MEA is that defined by Abu-Zahra et al. (2007) for 128°C, which may therefore be beneficial for the high-temperature cases. The use of multi-pressure strippers with vapour recompression was not considered, as the electricity demand would be almost doubled (Jassim and Rochelle, 2006). We use the standard configuration.

The stripper reboiler handles one evaporating stream (the absorption fluid) and one condensing stream (steam). The individual contributions from the evaporating and condensing streams to ΔT_{min} are 2.5 K, resulting in a minimum temperature difference of 5 K in the reboiler. Thus, the steam used to supply the heat to the reboiler is at a temperature of 95°C when the system is operating at 90°C. However, there are disadvantages associated with operating the steam system at sub-atmospheric pressure. Pipes that are pressurised to sub-atmospheric pressure levels are more expensive than pipes that are at atmospheric pressure, and the risk of leakage is greater. For the cases in which the flue gases from Chimney 4 or Chimneys 3 and 4 were treated, sufficient heat is available to produce an adequate level of steam at 100°C. The main advantage with this protocol is that sub-atmospheric pressure levels are avoided in the heat collection system. In addition, the area of the stripper reboiler is smaller due to the greater driving force. Given these benefits, it was decided that the heat collecting system should produce steam at a pressure of 1 bar in cases where the stripper reboiler is operated at 90°C if there is a sufficient amount of heat available at this temperature to sustain the operation.

4.2.2 Modelling the algae-based biofuel

An essential question in relation to land-based algae cultivation is how the heating of the pond can be achieved in a sustainable way. This is a main focus in **Paper IV,** where a heat balance is generated to estimate the heat demand of the algae cultivation pond for two growth rates: 12 g/m^2/day; and 40 g/m^2/day. As the pond is assumed to be well-insulated against the ground, the heat balance is calculated according to Eq. (1). The flow into the pond consists of water at 20°C.

$$Q_{pond,tot} = Q_{rad} + Q_{conv} + Q_{evap} \qquad \text{Eq. (1)}$$

where Q_{rad} denotes the incoming solar radiation, Q_{conv} denotes cooling due to convection, and Q_{evap} denotes the losses due to evaporation of the water.

This output is coupled to weather information, obtained from the Swedish Meteorological and Hydrological Institute (SMHI, 2011). The SMHI data contain the monthly average of wind, temperature, and precipitation values for Gothenburg in the period 2009–2011.

Marine-based cultivation does not encounter the same heating problem as the photobioreactors (microalgae); the ropes (macroalgae) have the same temperature as the ambient ocean. However, this does not ensure that the microalgae are exposed to the temperature for optimal growth.

Three different biofuel production routes from algal biomass are investigated: R1) lipid extraction for transesterification with subsequent anaerobic digestion of the algal residues; R2) HTL from a microalgal feedstock with subsequent CHG; and R3) HTL from a macroalgal feedstock with subsequent CHG. The modelling of the algae-based biofuel production routes is performed in Microsoft Excel, except for the calculation regarding the product output of the microalgae HTL, which is done in MATLAB. All production routes are modelled based on heat and electricity demand data from the literature, as this was considered to be the most consistent way to perform the analysis. The biofuel production routes are each evaluated from the CO_2 perspective, and with two different efficiencies:

- Process efficiency, which does not take cultivation and harvesting into account:

$$\eta_{process} = \frac{\sum_i \dot{m}_i \cdot HHV_i}{\sum_j \dot{m}_j \cdot HHV_j + \dot{W}_{el,proc.} + \dot{Q}_{proc.}} \quad \text{Eq. (2)}$$

- System efficiency, where all the energy inputs to the system are taken into account:

$$\eta_{system} = \frac{\sum_i \dot{m}_i \cdot HHV_i}{\sum_j \dot{m}_j \cdot HHV_j + \dot{W}_{el,proc.} + \dot{Q}_{proc.} + \dot{W}_{el,harv.} + \dot{Q}_{el,harv.}} \quad \text{Eq. (3)}$$

where *i* denotes the product streams, *j* denotes the input streams (i.e., biomass, diesel, and hydrogen), *proc* denotes the process demands, and *harv* denotes the cultivation/harvesting demands.

Using two efficiencies represents, to some extent, the benefits that could be achieved through process integration. Using previously un-utilised streams from the refinery to replace some of the inputs could increase process efficiency. The distinction between the two efficiency definitions is also made to indicate which parts of the system are the major bottlenecks for feasible and sustainable production of biofuels. For example, if the difference between $\eta_{process}$ and η_{system} is large, more research needs to be performed on the topics of cultivation and harvesting.

4.3 CO_2 emissions consequences

All the papers included in this thesis use an extended system boundary, which means that (for example) the electricity generation and heat production that occurs outside of the system (the oil refinery or the industrial cluster) but that is still used within the system affects the CO_2 balances. When adopting an expanded system boundary it is acknowledged that any one energy system affects another, and that all the energy systems are connected. This is common practice in energy system/LCA studies (Berlin et al., 2007; Zhang et al., 2014), and it has been used in the refinery industry, e.g., by Johansson et al. (2012) and Kuramochi et al. (2012).

Biomass is a limited resource, and the entire energy system is not renewable-based. If, for example, biogas is combusted instead of natural gas, this means that the biomass cannot be combusted anywhere else in the energy system and therefore gives rise to as much CO_2 emissions as would the burning of natural gas. Therefore, it doesn´t matter if the processes consumes natural gas while producing biogas or combusts some of the product gas if the entire energy system is not based on renewables.

Two levels of CO_2 emissions from electricity generation are used in this thesis, and they are assumed to be the results of the two scenarios presented in Section 1.1, the New Policy scenario and the 450 ppm scenario (Axelsson and Pettersson, 2014). The CO_2 emissions factors for each commodity are presented in Table 4.

Table 4: CO_2 emissions factors used in this thesis (Axelsson and Pettersson, 2014).

	CO_2 emissions (kg/MWh)
Electricity generation "New Policy scenario"	805
Electricity Generation "450 ppm scenario"	376
Heat generation (Heat-only boiler, fuelled with natural gas)	270
Replacement of diesel	284
Replacement of natural gas	224
Replacement of coal	364

CO_2 capture

With CO_2 capture, two measures are used: captured CO_2 and avoided CO_2. These two terms are explained in Figure 10. The reason for calculating both of these measures, instead of only calculating using the expanded system boundary (CO_2 avoided), is that the cost for the industrial plant (in this case, the oil refinery) can only affect the amount of CO_2 captured and can only be held accountable for the amount of CO_2 that is emitted on-site. Therefore, the costs also are separated into these categories (see Section 4.4)

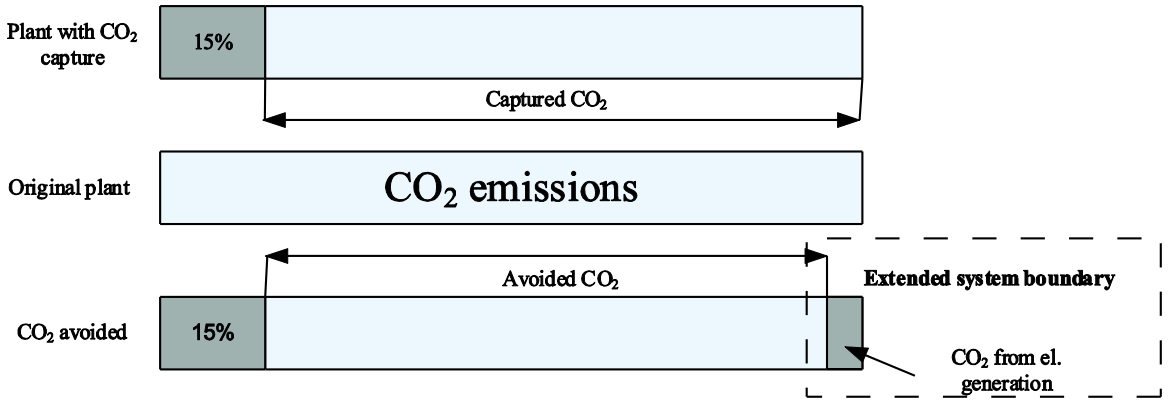

Figure 10: Explanation of the CO_2-captured and CO_2-avoided measures.

Algae-based biofuels

In the production of algae-based biofuels, the following flows are taken into consideration:

$$CO_{2,avoided} = \Delta CO_{2,ff} + \Delta CO_{2,proc}\{= \Delta CO_{2,el} + CO_{2,heat} + CO_{2,mat}\} \quad \text{Eq. (4)}$$

where $\Delta CO_{2,ff}$ denotes the change in CO_2 emissions when burning a biofuel instead of a fossil fuel, and $\Delta CO_{2,proc}$ denotes the CO_2 emissions associated with the process. $\Delta CO_{2,proc}$ is the sum of $\Delta CO_{2,el}$ (CO_2 emissions from electricity generation) plus $CO_{2,heat}$ (CO_2 emissions from heat generation) plus $CO_{2,mat}$ (CO_2 emissions from materials, such as hydrogen, methanol, and diesel).

4.4 Techno-economical evaluation

Paper III contains a techno-economical evaluation of CCS implementation through the MEA process at an oil refinery. There are several methods for calculating the increases in the costs of equipment over a time period, with two of the more common ones being: the Chemical Engineering Plant Cost Index (CEPCI); and the CERA Downstream Capital Cost Index (DCCI). Holmgren et al. (2015) compared these two indices and concluded that during the period 2007–2012, the indices showed a similar development pattern, indicating that the update in costs between those years is reliable. In the 10-year perspective, however, the two indices differed by up to 30%. This result accords with Vatavuk (2002) who concluded that updating cost estimates older than 5 years should be avoided. In this thesis, the CEPCI method is chosen, the base year is 2007, and the cost is updated according to the US dollar (US$) value in Year 2012, after which they are translated into Euro (€) using the currency exchange rate of Year 2012. Costs are calculated as described below.

Equation 5 is used to calculate the equipment cost for heat exchangers, towers, and pumps.

$$C_{eq} = (a + bS_0^n)(\frac{S_{eq}}{S_0})^{0.7} \quad \text{Eq. (5)}$$

The values of a, b, and n, which differ according to the type of equipment, are taken from Sinnott and Towler (2009). S_0 is the size parameter, e.g., the area for a heat exchanger (in m^2) in the model, and S_{eq} is the size of the actual equipment needed.

The cost C_{eq} includes only the actual equipment, and does not take into account installation, piping, and other associated costs. To account for these, the detailed factorial method proposed by Sinnott and Towler (2009) is used. This results in multiplying all the equipment costs by a factor of 6, to account for the associated costs. The total capital cost is then annualised using an annualisation factor of 0.13, which corresponds to an interest rate of 10 % and an economical lifetime for the plant of 15 years.

The cost for piping is estimated in consultation with a piping expert from the oil refinery, and can be found in the Supplementary information to **Paper III** (Hafström, 2015).

Two different costs are then calculated: the CO_2 capture cost and the CO_2 avoidance cost (see Figure 10). The CO_2 capture cost only takes into account the emissions that occur within the refinery site. Since no emissions are generated by the capture process (only excess heat is used), this cost is equivalent to what the refinery would have to pay, i.e., a cost that is interesting from the corporate point of view. In contrast, the CO_2 avoidance cost uses an expanded system boundary and thus takes into account the offsite emissions from the production of electricity that is used in the CO_2 capture process. This cost is more interesting from a research point of view, since it can be measured against other climate mitigation options. The above costs are defined as:

$$CO_2\ capture\ cost = \frac{Total\ cost\ for\ capture}{Amount\ of\ CO_2\ captured} \quad \text{Eq. (6)}$$

$$CO_2\ avoidance\ cost = \frac{Total\ cost\ for\ capture}{Amount\ of\ CO_2\ captured - Amount\ of\ CO_2\ emitted\ du\ to\ el.prod.} \quad \text{Eq. (7)}$$

4.5 Key assumptions made throughout this thesis

Throughout this thesis (**Papers I-V**), it is assumed that all the available excess heat can be utilised. Since detailed engineering has not been performed, the availability of space and the possibilities to utilise current pipe routes have not been investigated. Furthermore, the pipes of the heat collecting system are assumed to be so well-insulated that no heat losses occur (see **Paper III**).

The availability of excess heat is not varied throughout the season. Instead, E. Andersson et al. (2013) aimed at creating a snapshot that well represents the average function at the refinery. Seasonal variation arises in relation to the fact that it is more difficult to condense gases during the summer, i.e., the purge gas balance is changed, although this does not have a significant impact on the potential for process integration.

All the heat that is removed by the cooling utility is considered as "unavoidable" excess heat, i.e., the use of excess heat from the oil refinery is not encumbered with any CO_2 emissions.

All mentions of CO_2 emissions in this thesis relate to greenhouse gas emissions in CO_2-equivalent emissions.

A limitation of the CO_2 capture part of this thesis is that the "loading", which is the relationship between the amounts of CO_2 that are dissolved in the absorption fluids at the inlet and outlet ports of the absorption column, remains constant for all the tested temperatures.

During the work, the case study refinery has made several changes, most notably the substitution in the hydrogen production process of butane with methane, which has decreased the levels of CO_2 emissions and probably has also altered the amount of available excess heat. For consistency, the conditions that were valid at the beginning of the work have not been altered in this thesis.

As mentioned in Section 1.1, this thesis is based on two scenarios (out of three) created by the IEA. Since the WEO scenarios have a time horizon that extends only up to Year 2035, this thesis also uses this time-span (IEA/OECD, 2013). The policies that are assumed to be implemented are cumulative, i.e., the measures that are listed under the Current Policy scenario are also implemented in the New Policy scenario, where they are supplemented with new measures.

The **Current Policy scenario** is based on the existing policies and measures that have been implemented mid-2013. Clearly, this is not enough to decrease global CO_2 emissions, so it has been excluded from the thesis.

The **New Policy scenario** takes into account announced commitments, even if the specific measures to meet these commitments have yet to be introduced. It assumes a situation of "only cautious implementation of current commitments and plans". Notably, the US is not assumed to implement any new, cross-cutting policy changes and the EU is assumed to be only partially successful in reducing primary energy demand by 20% in Year 2020. By Year 2020, China is assumed to reduce the CO_2 intensity by 40% (as compared with Year 2005) and implement CO_2 pricing.

The **450 ppm scenario** is consistent with a 50% chance of meeting the goal of limiting the increase in average global temperature to 2°C, compared to pre-industrial levels. Up to Year 2020, the 450 ppm scenario assumes a policy action to implement fully the Cancun Agreement. After Year 2020, all the OECD countries and "other major economies" are assumed to implement economy-wide policies to meet the CO_2 emissions target for Year 2035.

The thesis considers a future up to Year 2035, in which a coal power plant and a natural gas combined cycle (NGCC) plant are assumed to be the build margin for the New Policy scenario and 450 ppm scenario, respectively (Axelsson and Pettersson, 2014).

Presented in Figure 11 are three possible trajectories for global CO_2 emissions after Year 2011, with one of the WEO scenarios represented by each line. For a more thorough description of the different scenarios, the reader is referred to WEO 2013 (IEA/OECD, 2013).

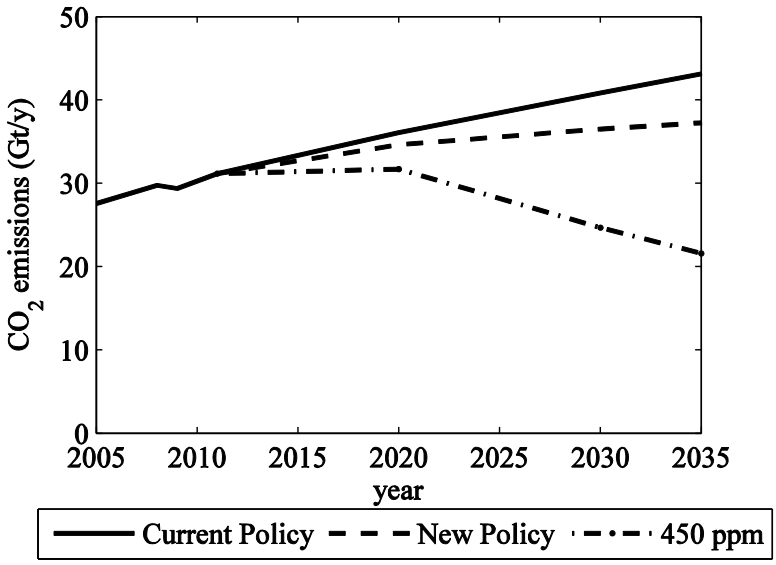

Figure 11: Historic CO_2 emissions and predictions up to Year 2035 of CO_2 emissions levels according to the WEO scenarios.

Figure 11 shows the global CO_2 emissions, as well as how fast the policy changes must be implemented if the 450 ppm scenario "only" is to be consistent with a 50% chance of actually limiting the increase in global temperature to 2°C.

4.6 Uncertainties linked to the input data and assumptions

Throughout this work, it is assumed that excess heat is free of both cost and CO_2 emissions. That excess heat is free of cost assumes that no customer is interested in other uses of the available excess heat. There are three main end-uses of excess heat:

- Internalisation of the heat by process intensification (recycling the heat back to the oil refinery processes)
- A nearby district heating network
- Another industrial plant being interested in buying low-pressure steam

If any of these three options are currently available the excess heat becomes associated with the cost that these entities are willing to pay for such excess heat. At the complex refinery, which is the focus of **Papers I-III** and **V,** this is currently not the case, although proposals have been made to connect the refinery to a district heating network located approximately 35 km away. The internalisation of heat through increased energy efficiency is promoted by the 450 ppm scenario, where it is foreseen that more than 50% of the CO_2 abatement will be the result of energy efficiencies (IEA/OECD, 2013). As soon as the heat can be used internally, it can be regarded as avoidable (Bendig et al., 2013), as illustrated in Figure 6, a and b. The assumption that excess heat, as defined in this thesis, will in the future continue to be cost-free is debatable and highly uncertain. Therefore, a sensitivity analysis is performed with regards to the cost of excess heat in **Paper III**, which is the only paper that considers the economic issues.

The assumption that the excess heat is not encumbered with CO_2 emissions is valid if it is "unavoidable" excess heat, in line with the discussion provided above.

Using the same lean loading may affect the result negatively in the low-temperature cases. In a parametric study performed by Abu-Zahra et al. (2007), it was shown that the optimised loading had a specific heat demand that was 11.5% lower than the base case. They also showed that the specific heat demand had a minimum of 0.32 mol_{CO2}/mol_{MEA}, and that in the lean loading interval of 0.28–0.36, there was almost no change in the specific heat demand. Another parametric study performed by Duan et al. (2012) found that if the lean loading was between 0.2 and 0.3 mol_{CO2}/mol_{MEA} the specific heat demand changed little in line with the lean loading used. The loading used in this thesis is that described by Abu-Zahra et al. (2007) to be the minimum, i.e., 0.32 mol_{CO2}/mol_{MEA}. The studies carried out by Abu-Zahra et al. (2007) and (Duan et al., 2012) suggest that there is an error associated with using the same loading for all temperatures, although such a small error does not change the results to a significant extent. Therefore, an optimisation study involving all three levels of stripper reboiler temperatures has not been performed, since it would take a lot of time and there are other, larger uncertainties linked to the input data, e.g. the heat mapping of the refinery.

5 Results and discussions of main findings

This chapter presents the results from the different studies, as described in the appended papers. The chapter is divided into the CO_2 capture results, algal biofuel results, and inte CO_2 emissions results.

5.1 CO_2 capture

5.1.1 CO_2 capture rate at a generic plant

The CO_2 capture rate of an industrial plant with access to excess heat depends on the temperature in the stripper reboiler, which affects both the change in specific heat demand and the amount of available excess heat. More heat is usually available at lower stripper reboiler temperatures, and it is common that the increase in available heat starts just below low-pressure steam temperature.

Specific heat demand vs. stripper reboiler temperature

Figure 12 shows the relationship between heat demand and the temperature in the stripper reboiler for the MEA process and the ammonia process. The modelling of the ammonia process was done by Jilvero (V. Andersson et al., 2014c; Jilvero et al., 2014b; Jilvero et al., 2012). The circles in the figure represent the measuring points at which the heat demand is modelled. Since the conditions for absorption were not changed, the absorption columns were not changed in the different configurations of the models.

The MEA model has been validated against the data of Abu-Zahra et al. (2007) down to 108°C, below which temperature it has been validated against the results of Dugas (2006). In accordance with expectations and the results from several other studies, the specific heat demand increases with decreasing temperature (Abu-Zahra et al., 2007; Duan et al., 2012; Dugas, 2006; Notz et al., 2012). The increase in heat demand seemingly levels out below 105°C; the ΔH value differs more when the temperature in the stripper reboiler decreases from 120°C to 105°C than when it further decreases to 90°C. The change in specific heat demand is approximately 40% when the temperature in the stripper reboiler is changed from 120°C to 90°C. For the ammonia process, the heat demand is almost linear until 120°C, increasing by 13% from the standard 155°C. at temperatures <120°C, the increase in heat demand to the next measurement point, at 105°C, is 45%.

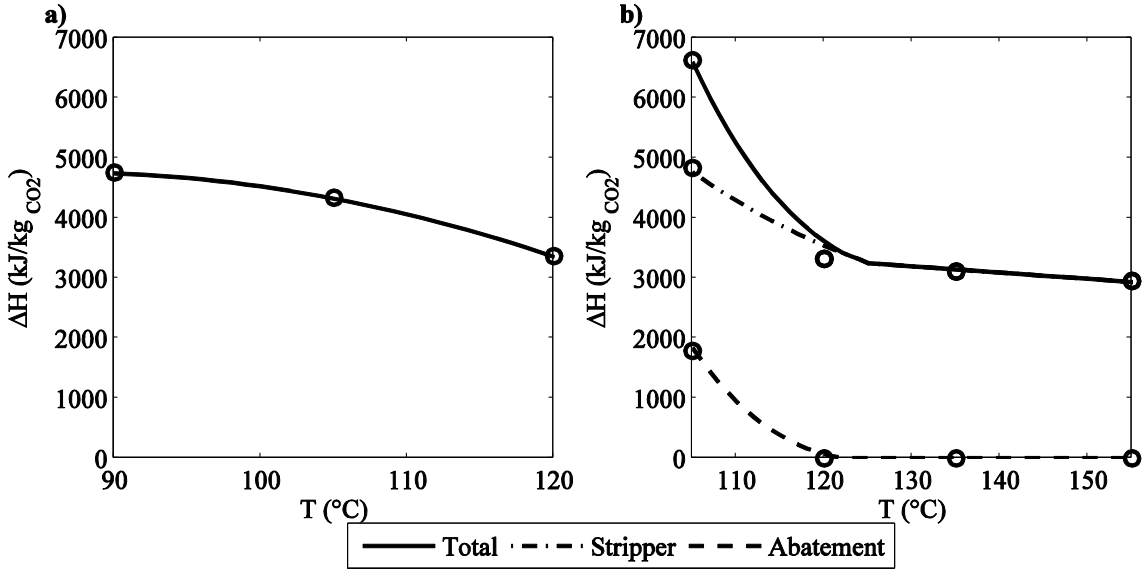

Figure 12: Specific heat demands for various temperatures ($T_{Reb.}$ values) in a stripper reboiler column used to regenerate: a) MEA; and b) ammonia. The results for the ammonia heat demand are courtesy of Dr. Jilvero.

Excess heat availability

While the change in specific heat demand appears to be large, the available excess heat also increases with decreasing temperature. As described in Section 3.1.1, a linear approximation of the ACLC in the temperature interval for each absorbent can be seen as a reasonable approximation for an early estimate of suitable absorbents.

Figure 13 presents the CO_2 capture rate for some of the Q_{add}/Q_{tot} ratios (defined and explained in Section 3.1.1) relative to the standard temperature (120°C for MEA; 155°C for NH_3) in the stripper reboiler. Note that only relative values are shown, i.e., the capture rate at the standard temperature can vary depending on the conditions used.

Figure 13a shows that it in most cases it is beneficial to decrease the stripper reboiler temperature of the MEA process to 90°C, due to the higher CO_2 capture rate at 90°C. The breaking point occurs at approximately Q_{add}/Q_{tot}=0.3, where the CO_2 capture rates at 120°C and 90°C are virtually identical. For Q_{add}/Q_{tot} ratios <0.3, the CO_2 capture rate at 120°C is higher than that at 90°C. For the ammonia process Figure 13b shows that from a CO_2 capture rate perspective, no Q_{add}/Q_{tot} ratio is able to decrease the stripper reboiler temperature to the lower boundary within the investigated temperature interval (105°-155°C). The temperature needed for maximum CO_2 capture is in the range of 112°–155°C; the higher the Q_{add}/Q_{tot} ratio the lower the temperature needed for the maximum CO_2 capture rate. That the maximum CO_2 capture rate never reaches the lower boundary of the temperature interval reflects both the increasing heat demand of the abatement cycle and the heat demand of the regular ammonia cycle.

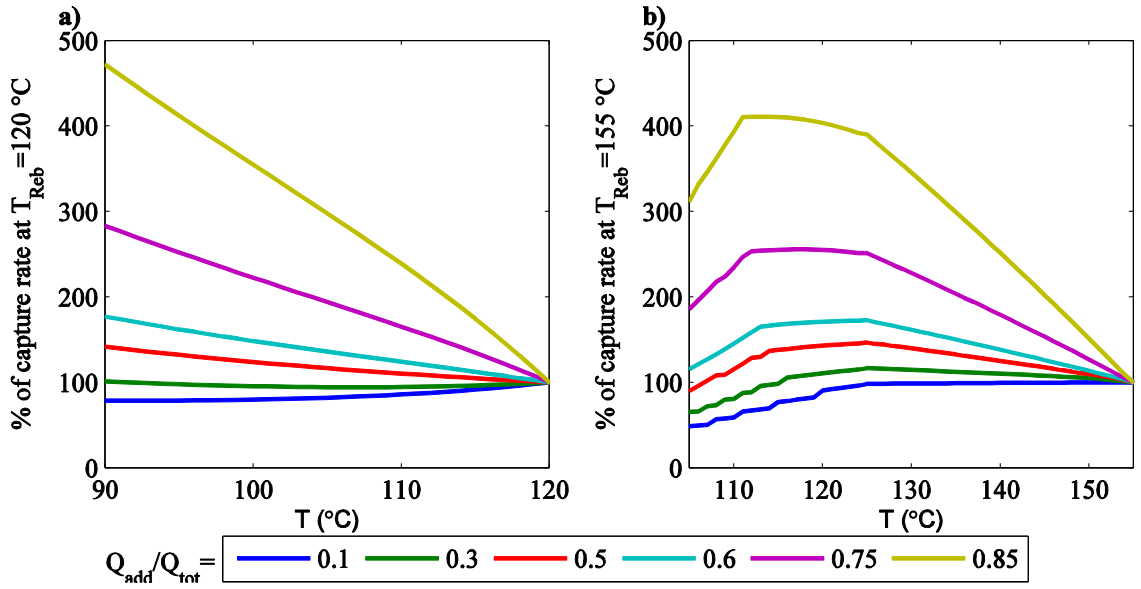

Figure 13: CO_2 capture rates for different Q_{add}/Q_{tot} ratios and temperatures in relation to how much CO_2 is captured at the standard temperature of a) 120°C (MEA) and b) 155°C (ammonia)

Figure 13 demonstrate some of the influences that the excess heat of an industrial process exerts on the choice of absorbent. The availability of excess heat can change the characteristics that are desirable in a CCS process. Dividing the heat demand (as in the ammonia process) into two separate temperatures (the abatement cycle and the stripper reboiler) could be beneficial. However, to attain these benefits, there needs to be a more even distribution between the two heat demands. The ammonia abatement cycle mostly exerts an influence at close to 105°C, which is too close to the abatement stripper temperature, which eliminates the possibility to improve heat integration with the oil refinery. To obtain access to sufficient levels of excess heat and CO_2 to motivate the inclusion of two strippers (e.g., in an industrial cluster), two different reboiler temperatures could be used, thereby facilitating the utilisation of a broader range of excess heat while maintaining high efficiency in the various parts of the process. The process would benefit from both the lower specific heat demand of the higher temperature and the additional available heat that is present at lower temperatures.

There is a trade-off between the desire to capture as much CO_2 as possible and ensuring ease of operation. This is valid for both the MEA and ammonia processes, albeit for different reasons. For MEA, it is mainly the increasingly sub-atmospheric pressure that causes problems, whereas for ammonia, it is the increasing ammonia slip. Modelling the MEA process at a stripper temperature of 90°C is associated with some uncertainty. As very little experimental work has been carried out at such low temperatures, the sources available for validation are limited. While some work in this area has been carried out, for instance by Dugas (2006), more in-depth studies are needed to operate successfully a full-size plant at this temperature. As the temperature for maximum capture rate is the boundary temperature, conducting experiments at temperatures below 90°C would be interesting, using MEA or other absorbents.

5.1.2 Case study results

Heat integration

Heat integration of a CCS plant in a refinery offers large savings in terms of the heat demand of the CCS process if the level of heat integration is high. Previous studies have examined the theoretical potentials for entire process sites, whereas this thesis concentrates on more modest levels of heat integration. Two levels of heat integration are investigated, i.e., replacing 10 or 30 heat exchangers (HX) in order to utilise excess heat. The chosen ΔT_{system} was 10 K. The ACLC for replacing 10 or 30 heat exchangers is shown in Figure 14. The figure is enlarged to show only the area relevant for heat integration.

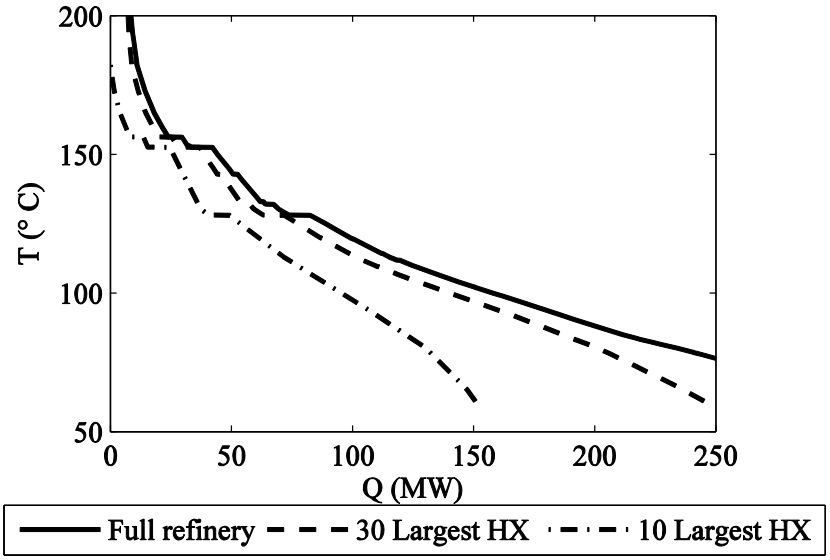

Figure 14: Available excess heat levels following the replacement of 10 or 30 heat exchangers (HX) at the case study refinery.

Figure 14 shows that the availability of excess heat for temperatures >110°C decreases to substantially between a case in which 30 heat exchangers are installed and a case in which 10 new heat exchangers are installed. In the case of 30 heat exchangers being replaced, the graph shows congruence with the graph for the full refinery down to 155°C where 90% of the full potential can be extracted. The divergence is increasing as the temperature and at 90 . Therefore, the case with 30 new heat exchangers is evaluated further, as it is deemed manageable to replace 30 new units.

Industry is sometimes wary of the practical constraints and costs for such a network. While a detailed engineering study was not performed, the results show that a targeted and limited heat exchanger network does not entail a significant reduction in the level of available excess heat. As shown in the economic evaluation, the heat exchanger network represents a minor cost fraction of the total cost for CO_2 capture. The network was cost-estimated using the methodology described in Section 4.4.

MEA or ammonia as absorbent

Figure 15 shows the amounts of CO_2 that can be captured at different temperatures of the stripper reboiler in the case study refinery. Ammonia has a wider temperature range for stable CO_2 recovery rate than MEA. Compared to the generic study, the temperature for maximal CO_2 recovery for the ammonia process is somewhat lower, since the case study ACLC is not linear in the ammonia temperature interval (see Figure 6b). The Q_{add}/Q_{tot} ratios are 0.55 and 0.85 within the temperature intervals for MEA and ammonia, respectively. This results for the stripper reboiler temperatures, for maximum CO_2 capture, are 90°C for MEA and 108°C for ammonia.

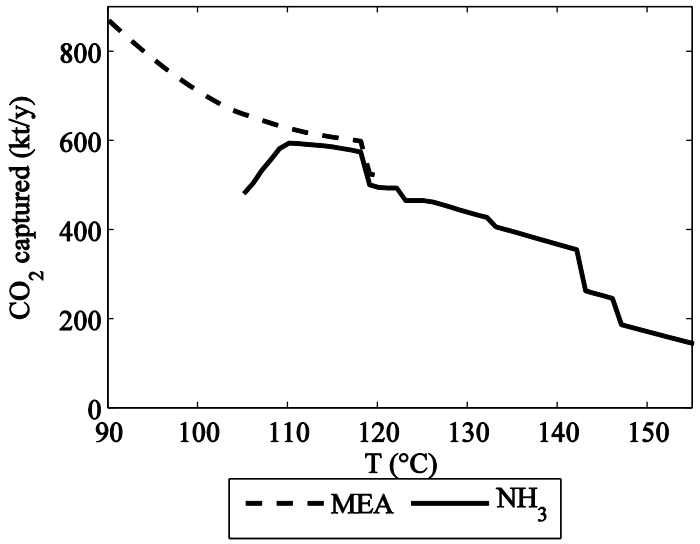

Figure 15: Levels of CO_2 that can be captured at the case study refinery using only excess heat at different temperatures in the stripper reboiler.

In Table 5, the modelled measuring points of the two processes are shown. Listed are the resulting heat demands of the two processes after heat integration. For 90°C, both the amount of heat available for extraction at a ΔT_{system} of 10K, and (in brackets) the available heat for production of steam at 1 bar are shown (see Section 4.2.1). Also presented in Table 5 are the amounts of CO_2 that can be captured for each level of available heat. The heat demands for MEA and ammonia are very similar at a stripper reboiler temperature of 120°C; due to curve fitting, the amounts of CO_2 captured are different.

Table 5: Heat demands after heat integration at the measurement points, and the availability of excess heat.

	90°C	**105°C**	**120°C**	**135°C**	**155°C**
Heat available for CCS integration (MW)	140 (124[2])	97	60	42	15
MEA					
Specific heat demand in reboiler (kJ/kg CO_2)	4 760	4340	3370	-	-
Amount of CO_2 that can be captured with only excess heat (Mt/year)	0.87 (0.78)	0.66	0.52		
Ammonia					
Specific heat demand in the reboiler (kJ/kg CO_2)	-	4840	3320	3110	2950
Specific heat demand in the abatement cycle (kJ/kg CO_2)	-	1790	0	0	0
Amount of CO_2 that can be captured with only excess heat (Mt/year)	-	0.48	0.50	0.4	0.15

As the results show, the absorbents that can operate at low reboiler temperatures are beneficial for industrial applications that have access to excess heat. The advantage associated with the lower heat demand of ammonia at high operating temperatures is cancelled out by the fact that the MEA process is able to decrease the temperature further in the stripper reboiler. For the MEA process, there is a boundary solution at the lower boundary of the temperature interval, whereas for the ammonia process, the extra heat gained at temperatures <120°C (compared with having a linear approximation of the ACLC in the temperature interval) reduces the temperature for maximum CO_2 recovery. However, the level of abatement heat eventually becomes too high for it to be a boundary temperature solution.

Economic evaluation of the MEA process

The MEA process was selected for a techno-economical analysis to elucidate the economic benefits of using excess heat. The analysis is performed on four cases in a two-by-two matrix, whereof the temperature constitutes one dimension. The chosen temperatures are 90°C and 120°C. The second dimension is how many chimneys from which the flue gases are treated. The results of the economic analysis are divided into capital costs (CAPEX) and operational costs (OPEX). A summary of these costs is shown in Table 6.

[2] Heat available to make 1 bar steam according to the discussion in Section 4.2.1.

The different cases (A and B) are as follows:

- **A.** Flue gases from Chimneys 3 and 4 are in focus. Chimneys 3 and 4 are the two chimneys that have the highest CO_2 concentrations in their flue gases, so this case entails flue gases the relatively high purity level of 20% CO_2. The heat demand for capture of 85% of the CO_2 from Chimneys 3 and 4 also approximately match the availability of excess heat for separating 85% of the CO_2 emissions at a stripper reboiler temperature of 90°C with 1 bar steam, as shown in Figure 16. Case **A** results in the capture of 40% of the total refinery CO_2 emissions.
- **B.** Only the flue gas from Chimney 4 is considered. Chimney 4 has the highest flue gas CO_2 concentration of the four chimneys, so this case entails flue gases of even higher purity: 24% CO_2. The heat demand for capture of 85% of the CO_2 emissions from Chimney 4 approximately matches the availability of excess heat at a stripper reboiler temperature of 120°C, as shown in Figure 17. Case **B** results in the capture of 28% of the total CO_2 refinery emissions.

The levels of excess heat available at the refinery are such that only two of the four chimneys that are deemed suitable for CO_2 capture (Section 3.1.1) are actually used. For the economic results pertaining to the CO_2 capture of all four chimneys, see **Paper III**, where heat pumps are used to supply supplementary heating.

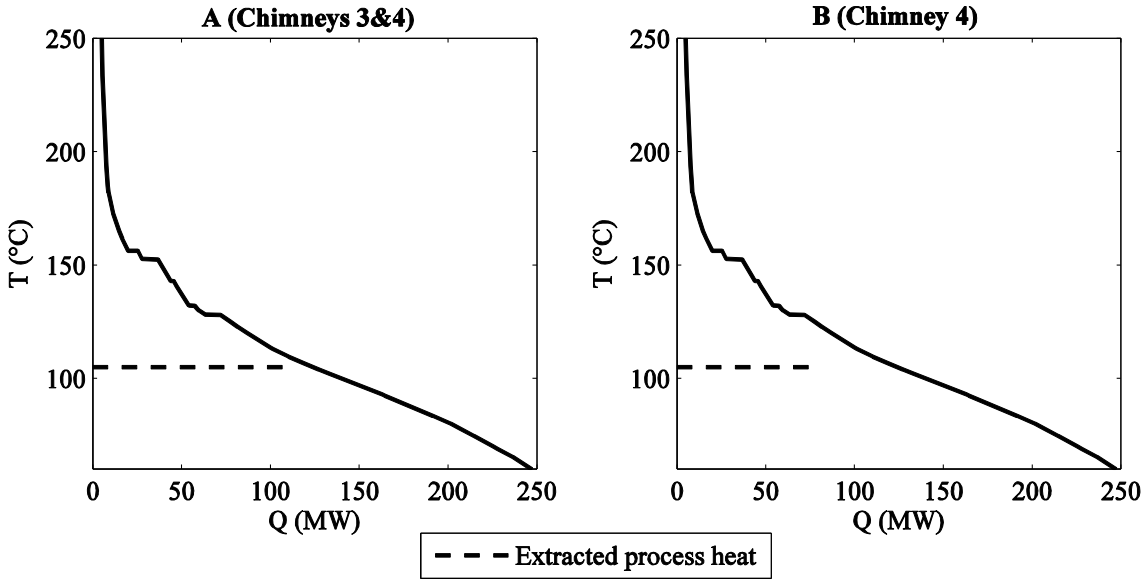

Figure 16: Heat levels that can be supplied in cases with a temperature of 90°C in the stripper reboiler. The line representing the extracted heat is located at the target temperature of the refinery process streams.

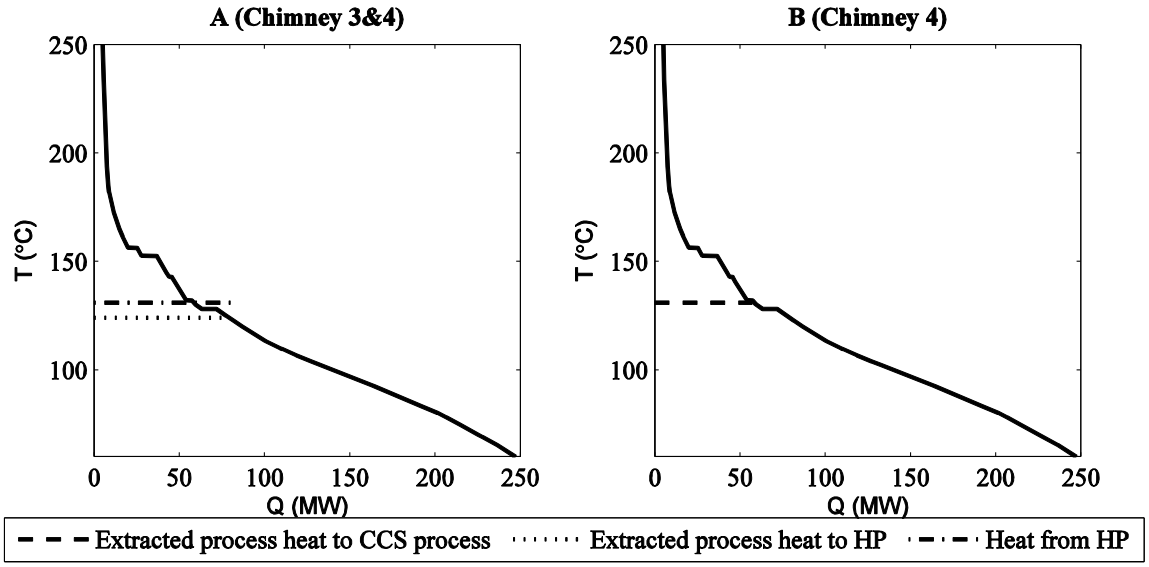

Figure 17: Heat levels that can be supplied in cases with a temperature of 120°C in the stripper reboiler. The line representing the extracted heat is located at the target temperature of the refinery process streams.

Figure 17 illustrates that in Case A, with a stripper reboiler temperature of 120°C, all the heat is supplied *via* a heat pump. Because the temperature increase is so small (113°C →125°C), it is deemed beneficial to have only one system that supplies the heat. The COP of the heat pump is 19.3, and the electricity demand is 3.5 MW.

According to current policies, industrial sites are responsible only for the CO_2 that they emit onsite. Thus, the price for emitting CO_2 must be compared to the cost for capturing CO_2 onsite and not compared to the globally avoided CO_2, which considers both onsite and offsite emissions. The breakdown of the subcategories in Table 6 relates to onsite avoided CO_2. The difference in cost between CO_2 avoided onsite and CO_2 avoided globally is shown in Table 6.

The capital cost per tonne of CO_2 captured is very similar for the different cases. Operational costs are mainly related to electricity used for the compression and for the MVR, as well as for the absorber/stripper. The heat-collecting system contributes 7%–16% to the CAPEX, if one includes the heat pump needed to separate 85% of the CO_2 in Case A with a stripper reboiler temperature of 120°C. The percentage relevance of the CAPEX is increased when the large cost of heat disappears from the OPEX.

Table 6: CAPEX and OPEX cost breakdowns. The total CAPEX and OPEX costs are listed, as well as the percentage of the total cost divided into subcategories for the onsite avoided case.

Case A=Chimneys 3 and 4 Case B=Chimney 4	**90°C Case A**		**90°C Case B**		**120°C Case A**		**120°C Case B**	
Captured amount of CO_2 (kt/y)	710		510		710		510	
Absolute Costs								
CAPEX (M€)	130		98		137		96	
OPEX (M€/y)	12.1		8.7		13.0		7.5	
Specific costs (€/t)								
CO_2 captured	41		42		39		43	
Scenario	NP	450	NP	450	NP	450	NP	450
CO_2 avoided	50	44	48	45	45	42	52	47

NP, New Policy scenario; 450, 450 ppm scenario.

When the heat demands of the two stripper reboiler temperature levels can be covered simply with excess heat, the lower compression cost makes it beneficial to operate the reboiler at 120°C. For the B cases (both stripper reboiler temperature levels can use 100% excess heat), the cost benefit of using the higher temperature level is 3 €/t. In contrast, for Case A, it becomes 2 €/t less expensive to operate at 90°C (a heat pump is needed when operating at a stripper reboiler temperature of 120°C). This is the main difference in cost shown in this thesis, and this shift in cost benefit highlights the importance of using excess heat. While the numbers should be considered as estimates, it is clear that the utilisation of excess heat yields a significant reduction in cost compared to, for example, a boiler. When using excess heat the cost differences are very small between both the different stripper reboiler temperatures and the different cases investigated.

The difference between CO_2 globally avoided and CO_2 onsite avoided is that offsite emissions (e.g., electricity production) are included in the globally avoided cost. The difference in cost is in the range of 3–4 €/t in the 450 ppm scenario, and could be within the error of uncertainty. For the New Policy scenario, the difference in cost in the range of 6–9 €/t, representing 15%–25% of the overall cost. It is important to be able to compare the results from different papers. In this thesis, an underlying assumption when estimating the refinery avoidance cost is that all the costs for emitting CO_2 during electricity generation are covered from the producer level, and therefore this is included in the price of the electricity.

The pre-conditions for the economic part of this study were small differences in both CO_2 concentration, and the amount of flue gas to be treated. Ho et al. (2011) concluded that the difference in cost between a refinery and a coal power plant was 17 US$ (70 US$ for the coal power plant and 87 US$ for the refinery); however, in their study, both the CO_2

concentration and the scale benefits were on the coal power plant side (13% CO_2 and 3 Mt/y for the coal power plant; 9% CO_2 and 1 Mt/y for the oil refinery, respectively). Husebye et al. (2012) showed that the difference in cost for carbon capture was larger when alternating between 3% and 10% than between 10% and 20% CO_2 in the flue gases. In this thesis, the concentration of CO_2 varies between 20% and 24%, and the cost benefits of increasing the CO_2 concentration would likely be larger at plant sites where no high concentration units are present for example oil refineries without a steam reformer. In addition, as noted by Kuramochi et al. (2010), scaling up is only beneficial to the point where the maximum size of one process line is reached. The benefit of scale disappears when duplicated into two parallel equipment lines.

5.2 Algae-based biofuels

5.2.1 Integration of land-based cultivation systems and area efficiency

In **Paper IV**, it was investigated how a large land-based cultivation area for microalgae is needed to treat the entire wastewater produced by Gothenburg. The area required for algae cultivation varies with the growth rates of the algae. The resulting pond sizes and the specific areas are listed in Table 7, together with the matching of available excess heat from the two refineries versus the heat demand of the pond.

Table 7: Algal growth rates and the corresponding required pond sizes for the utilisation of all sewage sludge produced at Gryaab.

Algal growth rate (g/m^2/day)	12	40
Pond size (km^2)	7.2	2.2
Growth rate that can be achieved	March–September	June–July
Period during which no excess heat is needed	March–September	
Periods during which excess heat is needed and is sufficient	October	October–November January–February
Period during which excess heat from the refineries is needed but is insufficient	November–February	October–February

As shown in Table 7, the months during which even the low growth rate cannot be achieved overlap with the months during which the industrial excess heat is not sufficient to heat the pond. There are major uncertainties regarding how the growth rate of the algae is affected by the climatic conditions in Gothenburg. The broad growth range of 12–40 g/m^2/day leads to uncertainties regarding the area efficiency and the heating requirements for the pond. Supplementary light and heat would probably have to be supplied to maintain full operation year-round. Therefore, it could be argued that seasonal production would be more suitable

for Gothenburg. As the cultivation of algae would supposedly replace the WWTP, this means that either the WWTP is used for some part of the year or a storage facility would have to be built to store the untreated wastewater. Since wastewater passes through Gryaab at a rate of 3.8 m^3/s, storage is not a feasible option. The average growth rate of the algae over a full year is 20 g/m^2/day, which is achievable in the period of April–September.

A comparison of the area efficiencies of algae-based biofuels with those of other biofuels, taken from Börjesson (2007), is illustrated in Figure 18. It should be noted that the values given are gross outputs and not the net yields. It can be seen that algae-based biofuels yield between 7–31-times more biofuel per hectare than the closest competitor, biogas from sugar beets. This assumes operation of the algae pond throughout the year. The processes with three algal strains depicted in parentheses are the routes evaluated in **Paper V**, and the area derived efficiency is only a preliminary estimate (see Supplementary Information to **Paper V** for the respective calculations). When comparing the yields in Figure 18 for the algae cases with low and high efficiencies with the experimental values obtained in Paper V, the high efficiency case appears to be too optimistic for year-round production.

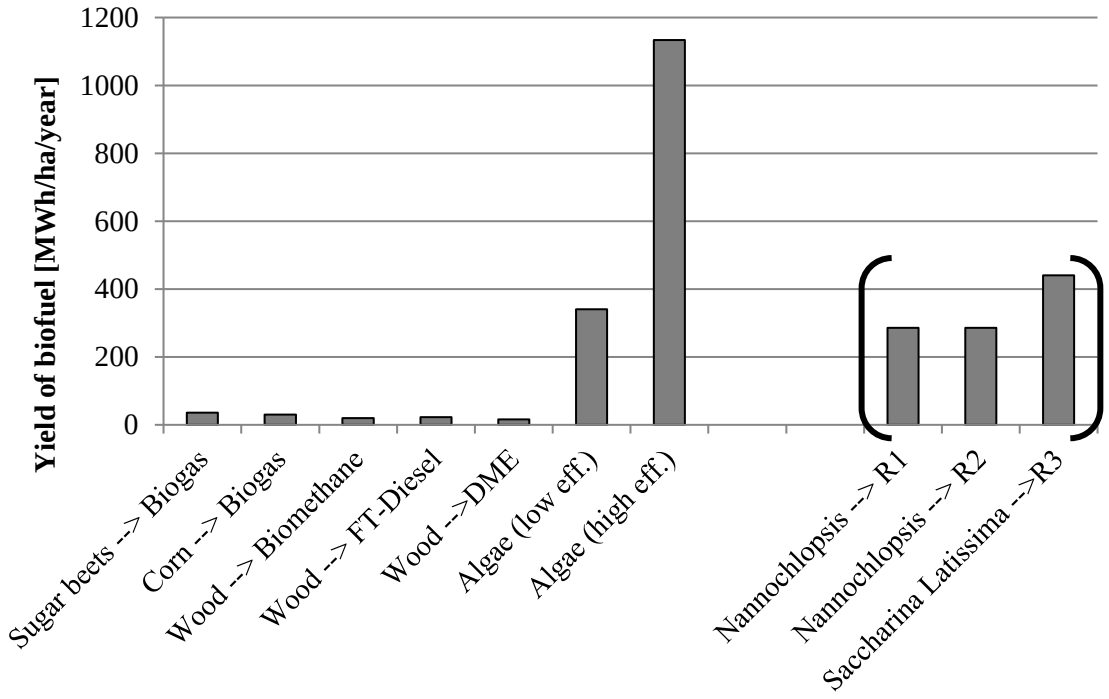

Figure 18: Area efficiency of different biofuel routes, non-algae biofuel routes are taken from Börjesson (2007). In parentheses are the strains used in **Paper V**, and the area efficiencies given are preliminary. See the Supplementary Information in **Paper V** for the respective calculations. R1, production of biodiesel and biogas from microalgae through lipid extraction; R2, production of renewable diesel and biogas from microalgae through HTL; R3, production of renewable diesel, biogas, and biochar from macroalgae through HTL

The area efficiencies of algae-based biofuel are, given the assumptions made in **Paper IV**, superior to those of other second-generation biofuel routes, such as wood-based gasification and Fischer–Tropsch diesel. The difference in area efficiency is smaller than that estimated by Williams et al. (2009), who suggested that algae biomass was 100– 300-

times more efficient than terrestrial biomass, but is larger than in the difference reported by Clarens et al. (2010), who performed an LCA on biomass growth but did not include the biofuel production step. Nevertheless, the area needed for algal cultivation is vast, and since municipal wastewater treatment (WWT) takes place in populated areas this could make the capital costs for ponds unfeasibly large. The geographical location may also render difficult the supply of heat to the pond, despite the presence of two refineries in the industrial cluster. The two refineries available on Hisingen in Gothenburg are not sufficient for heating the pond to a constant temperature of 20°C year-round. In the absence of excess heat, the entire amount of heat required for cultivation would have to be supplied by an alternative source, which would increase substantially the use of primary energy in the process, thereby altering the carbon balance. For these reasons, land-based algal cultivation in Gothenburg, without the use of industrial excess heat, can be ruled out.

The technologies assumed for the cultivation and harvesting of algae in this thesis are not yet fully developed. A key issue for algal cultivation is how to store the macroalgae without reducing the quality level. The lack of large-scale facilities means a lack of reliable data, a problem that has also been discussed by Olguín (2012). Future research on algae-based energy is, therefore, dependent upon the use of demonstration plants. As these plants are built and knowledge increases, the efficiency of the technology may increase and production costs decrease.

5.2.2 Integration of biofuel production processes

As the industrial excess heat was not suitable for land-based cultivation of microalgae, **Paper V** integrates the biofuel processes rather than the algal cultivation. The cultivation described in **Paper V** is marine-based, with three different routes from algal biomass to biofuel: R1, which produces biodiesel and biogas from microalgae through lipid extraction; R2, which produces renewable diesel and biogas from microalgae through HTL; and R3, which produces renewable diesel, biogas, and biochar from macroalgae through HTL.

As with the integration of the oil refinery with carbon capture and land-based algal cultivation, the main focus is on heat integration. There are, however, also mass integration aspects that need to be taken into account. Already mentioned are the co-locating benefits of using the CO_2 in the refinery flue gases for microalgae cultivation. The production of biogas can partly satisfy the methane demand of the refinery, and the biofuel plant can benefit from the large scale in terms of the produced biodiesel. In addition, the biofuel plant can use hydrogen from the refinery to improve system efficiency. A best-case scenario would be if the hydro-treater could use low-to-medium grade hydrogen, although the hydrogen could be produced elsewise using steam reforming instead of electrolysis (see Section 3.2.5).

While product output is calculated as a percentage of the algal biomass, it is converted to MJ per kg of algal biomass, as shown in Table 8.

Table 8: Product output, energy demands, and CO_2 emissions consequences from processing 1 kg of algal biomass (including moisture) in a stand-alone unit.

	Lipid extraction (R1)	**HTL microalgae (R2)**	**HTL macroalgae (R3)**
Product output (MJ/kg$_{algae}$)			
Bio/Renewable diesel	6.5	9.1[3]	2.7[4]
Biogas	9.6	4.1[3]	2.6[4]
Biochar	-	-	3.4[4]
Demands (MJ/kg $_{algae}$)			
Electricity demand	6.8	5.7	1.9
Heat demand	2.4	0.8	0.9
Fuel demand, diesel	-	-	0.7
Hydrogen demand	0.6	1.8	0.6
Methanol demand	0.6	-	-
Efficiency of process (%)			
$\eta_{process}$	**56**	**49**	**52**
η_{system}	**36**	**30**	**39**
Heat integrated			
$\eta_{process}$	**64**	**51**	**57**
η_{system}	**39**	**31**	**41**
Heat and material integrated[5]			
$\eta_{process}$	**69**	**63**	**63**
η_{system}	**41**	**35**	**44**

The compositions of the yielded products are diverse. Whereas R2 has the highest yield of renewable diesel, the highest yield of biogas is achieved through R1. In a stand-alone unit, some of the biogas would be combusted to supply the process with steam.

In comparing the process and system efficiencies, R3 shows a difference of 13%, whereas R1 and R2 show difference of 20% and 19%, respectively. The less-pronounced difference in efficiency observed for R3 is attributed to both a lower demand for electricity and an overall lower energy demand for the cultivation and harvesting processes. Utilising the excess heat from the oil refinery improves the system efficiencies of all three routes by 1%–3%, as compared with a stand-alone unit. However, the addition of material integration

[3] Based on the kinetic model of Valdez et al. (2014) using the composition of *Nannochloropsis* from Biller and Ross (2011)

[4] Re-calculated output from Anastasakis and Ross (2015, 2011)

[5] Assuming that the oil refinery´s steam reformer is used to produce hydrogen.

through utilisation of the refinery´s processes yields an improvement in system efficiency of 5% for all three routes.

To illustrate how the biofuel processes can be heat-integrated with the refinery, a background/foreground analysis is depicted in Figure 19; an input to the process of 100 MW_{algae} is chosen as an illustrative base case. The solid curve in the figure represents the aggregate excess heat from the refinery that is available for process integration. This represents the background process and does not change among the different cases. The *x*-axis is considerably different between the graphs, to enhance readability. The background process is still the same for all cases, although for R2 and R3, only the excess heat at the high-temperature level is depicted, as it is relevant to the integration of these routes. The overlap between the solid line and the dashed line (the biofuel process) represents the amount of heat that can be re-used.

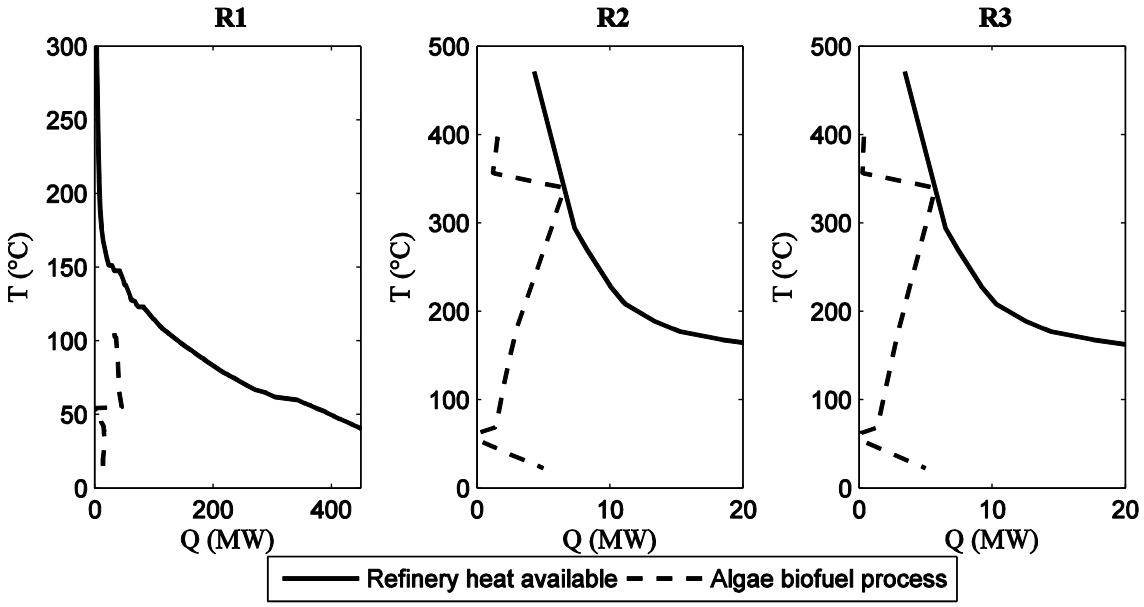

Figure 19: Illustrations of how the algae-based biofuel processes can be heat-integrated with the refinery. The overlap between the solid line (the refinery hot streams that need to be cooled) and the dashed line (the biofuel process) reflects the amount of heat that can be re-used.

When comparing the energy demands of the two main processes, lipid extraction and HTL, the most prominent differences observed relate to the heat integration possibilities and temperature levels. The heat integration analysis shows that R1 can be completely integrated with the refinery. Due to the lower temperature of the biodiesel process, the saving is approximately 45 MW for a 100-MW plant. There is also heat available for expansion of the process if more biomass is available. Approximately 2 MW of excess heat at a sufficiently high temperature is available to cover approximately 40% of the heating demand of either R2 or R3. To build a complete heat collection network for installation of approximately 2 MW of heat integration would not be an option. Further analysis of the refinery heat data shows that all of the heat that can be recovered for R2 or R3 is from a single heat source, i.e., one of the chimneys. The chimney is also conveniently located close to the potential site of the biofuel production process (Andersson et al., 2014b)e. Therefore, it is possible to integrate the biofuel production process.

A review of the current literature regarding algae-based biofuels shows that most of the studies have investigated microalgae. There are, however, seemingly several advantages associated with the use of macroalgae, including less-sensitive cultivation and easier harvesting. The main problem with macroalgae lies on the product side. As the overwhelmingly majority of transport vehicles currently run on liquid fuels, refinery companies want to produce liquid fuels so as to ease the transition towards biofuels and exploit the existing infrastructure. HTL from microalgae produces approximately 3.4-times more liquid fuel than HTL from macroalgae, and 2.4-times more liquid fuel than traditional lipid extraction.

Basing the biofuel process on macroalgae also entails benefits from the societal and environmental perspectives. Macroalgae do not need to be supplied with nutrients in the way that microalgae do; they reduce eutrophication by removing nutrients from the ocean. When implementing cultivation that corresponds to 100 MW of biomass, the macroalgae take up nutrients equivalent to the output of a wastewater treatment plant for a city with 600,000 inhabitants (Andersson et al., 2014a; Neveux et al., 2014). This creates an incentive from the governmental perspective to grow algae in oceans that are heavily eutrophic, e.g., the Baltic Sea. However, microalgae need nutrients to maintain their growth. To ensure sustainable cultivation, nutrients would have to be supplied from, for example, wastewater treatment. If the cultivation needs to take place in proximity to a CO_2 source, wastewater source, and heat source to be sustainable, the number of suitable locations shrinks. An underlying assumption of **Paper V** is therefore that normal wastewater treatment takes place, and that the sludge (corresponding to the make-up flow of nutrients) is thereafter transported to the algal cultivation site, since sludge is more easily transported than a large volume of wastewater. This means that the only additional impact on the environment would be the transport of the sludge, which is omitted in **Paper V** as it is deemed to have a minor impact on the results. If the cultivation of algae could be used to replace some part of the wastewater treatment, which would require the cultivation site to be located close to a city, both the carbon and energy balances would be altered (Andersson et al., 2014a).

5.3 CO_2 emissions consequences

The future electricity generation build margin is the main reason for basing the CO_2 calculations on two different IEA scenarios. As it is not possible to predict with accuracy the future build margin, it is important to investigate whether the system is robust in terms of CO_2 reduction when taking different technologies into account.

CO_2 capture

The first parameter to be investigated when evaluating different levels of temperature in the stripper reboiler is the amount of CO_2 that can be captured at each temperature. Since temperature and pressure are coupled, when the temperature is decreased the pressure is also decreased. The resulting pressure level when the temperature in the stripper reboiler is lowered from 120°C to 90°C leads to a significant increase (about 30%) in compressor power. As mentioned in Section 4.3, there is a difference between the amounts of CO_2 captured and CO_2 avoided, as the expanded system boundary takes the CO_2 emissions from

electricity generation into account. In Figure 20, the relationships between the amounts of CO_2 captured and CO_2 avoided are shown.

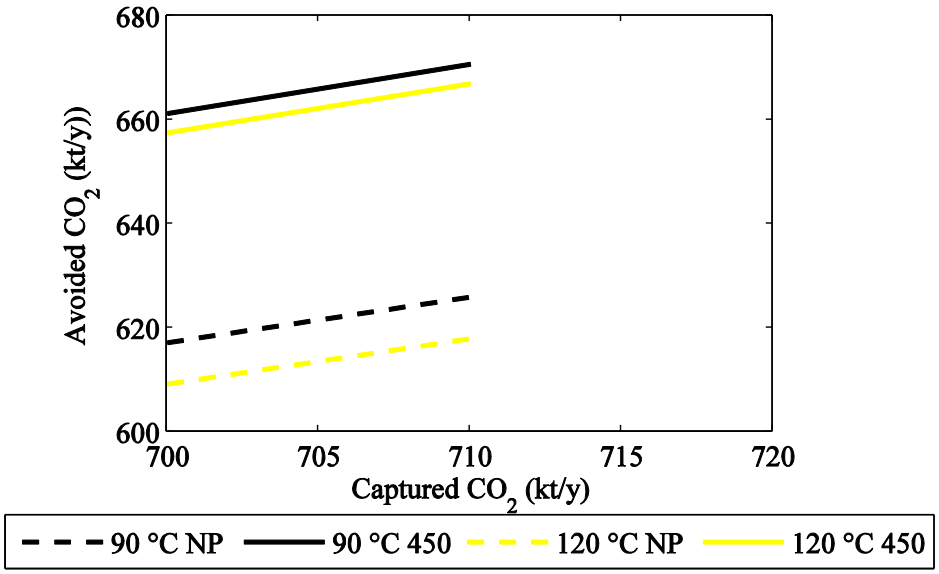

Figure 20: CO_2 avoided versus CO_2 captured in a stripper boiler operated at different temperatures and in two different scenarios. NP, New Policy scenario; 450, 450 ppm scenario.

Figure 20 shows that with a stripper reboiler temperature of 90°C, the resulting lower pressure leads to an increased use of electricity, which counteracts to a large extent the phenomenon that more CO_2 can be captured using only excess heat. The difference in amount of CO_2 avoided between the New Policy scenario and the 450 ppm scenario is approximately 45–50 kt_{CO2}/y. The difference in the amounts of CO_2 captured and CO_2 avoided between the two stripper reboiler temperatures is 8 kt_{CO2}/year for the New Policy scenario and 4 kt_{CO2}/year for the 450 ppm scenario. Therefore, there are other issues that dictate the choice of temperature level, e.g., cost, corrosion, and ease of operation. A stripper reboiler temperature of 90°C is marginally cheaper according to the techno-economical study made in Section 5.1.2, whereas more knowledge is gathered at the standard temperature of the stripper reboiler.

An important issue to consider is the time perspective. Figure 11 shows the CO_2 emissions until Year 2035, where NGCC is still on the build margin for electricity production for the 450 ppm scenario (Axelsson and Pettersson, 2014). After Year 2035, the CO_2 emissions will have to continue to decrease, which means that the electricity grid will be directed towards increasing use of low-carbon technologies. Therefore, once the shift to more low-carbon sources in the electricity system begins, the focus will shift towards maximising the CO_2 capture rate, and the need for compression will become less important. Once the build margin is a renewable technology there will be no extra CO_2 emissions from the electricity production that drives the compressors. Furthermore, industrial sites, such as oil refineries, have increasing levels of available excess heat at lower temperatures ($T_{Reb.}$=120 °C, Q=60 MW; $T_{Reb.}$=90 °C, Q=140 MW; $T_{Reb.}$=60 °C, Q=225 MW, at the complex refinery used as the case study in **Papers I-III** and **V**). These are two factors that underline why further reduction of the temperature in the stripper reboiler is important for MEA research, as well

as the need to develop novel absorbents that can absorb CO_2 at atmospheric pressure and low temperature.

Algae-based biofuels

Since a biofuel process needs to be of large size to be efficient, the CO_2 consequences per kg of algae, as well as for a 100-MW_{algae} plant are calculated for all three routes. The calculations are made for a stand-alone plant, as well as for an integrated plant, as shown in Table 9. For the integrated plant, it is assumed that the biofuel processes have been heat-integrated as far as possible, and that the hydrogen is produced *via* a steam reformer.

Table 9: CO_2 emissions consequences for the three routes investigated in **Paper V**.

	R1		**R2**		**R3**	
CO_2 balance (kg_{CO2}/kg_{algae})						
Product substitution ($\Delta CO_{2,ff}$)	1.13		0.94		0.72	
Stand-alone plant	**NP**	**450**	**NP**	**450**	**NP**	**450**
Process emissions ($\Delta CO_{2,proc}$)	-1.70	-0.89	-1.34	-0.66	-0.54	-0.32
CO_2 avoided	-0.57	0.23	-0.40	0.28	0.18	0.40
Heat- and mass-integrated plant	**NP**	**450**	**NP**	**450**	**NP**	**450**
Process emissions ($\Delta CO_{2,proc}$)	-1.52	-0.71	-1.27	-0.60	-0.48	-0.25
CO_2 avoided	-0.40	0.42	-0.34	0.34	0.25	0.48
100-MW_{algae} Plant						
CO_2 balance (kt CO_2/y)						
Product substitution ($\Delta CO_{2,ff}$)	198		165		175	
Stand-alone plant	**NP**	**450**	**NP**	**450**	**NP**	**450**
Process emissions ($\Delta CO_{2,proc}$)	-299	-157	-235	-116	-132	-77
CO_2 avoided	-101	41	-70	49	43	98
CO_2 balance (kt CO_2/y)	**NP**	**450**	**NP**	**450**	**NP**	**450**
Process emissions ($\Delta CO_{2,proc}$)	-267	-125	-228	-109	-120	-65
CO_2 avoided	-69	73	-63	56	55	110

Owing to its low electricity demand, R3 is the only route that shows a net CO_2 reduction for both the New Policy and the 450 ppm scenarios. The lower electricity demand for R3 is due to the lower demands of macroalgae cultivation and harvesting, although in terms of CO_2 levels, the difference is partly counteracted by the demand for diesel in the harvesting process. All the investigated routes show reduced emissions of CO_2 in the 450 ppm scenario. The resulting lowered CO_2 emissions from the system increase when utilising excess heat from the oil refinery, which is an advantage of R1, as it can be fully heat-

integrated. The recycled heat amounts to 45 MW, compared to 2 MW for R2 or R3, for a plant size of 100 MW_{algae}.

Preliminary estimates show that for cultivation corresponding to 100 MW of microalgae biomass, an area of approximately 27 km^2 would be needed for cultivation[6]. The cultivation must be near the shore because nutrients need to be pumped out through pipelines, and must occur in proximity to the site because microalgae have a dry solids content of approximately 5% when harvested, which would require large pipelines for transport. The need for pipelines results in logistical and spatial problems. The CO_2 that is being bubbled through the photobioreactors constitutes 6% of the CO_2 emissions of the refinery. This is not to be confused with CO_2 utilisation where CO_2 can be used for other purposes, e.g., enhanced oil recovery, which is just a speeded-up version of the normal carbon cycle.

For macroalgae, a cultivation area of approximately 13 km^2 would be required to generate a feedstock flow of 100 MW. Macroalgae cultivation does not have the same need to be located in proximity to the shore as does microalgae cultivation.

Nutrient supply could prove to be a crucial parameter for microalgae-based biofuels if it is encumbered with CO_2 emissions. In this thesis, the assumption is made that industrial flue gases can provide the necessary CO_2, and a nearby WWTP can transport the remnants of the treatment process (sludge) as a feedstock for the algae cultivation. In **Paper IV**, it is shown that a reduction of 14 kt_{CO2}/y could be achieved if microalgae cultivation was to replace conventional WWT.

[6] For area calculations of both microalgae and macroalgae cultivation, see Supplementary Information in **Paper V**.

6 Discussion of the cross-cutting issues from the results

In this chapter, the two themes of this thesis are discussed in relation to each other.

A large pulp and paper mill in Sweden has approximately 600 MW of biomass input. If a macroalgae-based biorefinery was to be implemented, approximately the same biomass input would be required to achieve the same CO_2 emission reduction (in the 450 ppm scenario) as the CO_2 captured from two of the case study refinery´s chimneys. While the cultivation of algae is area-efficient, it would still require vast surface areas (approximately 78 km^2) to ensure that this amount of biomass input would be produced. It is reasonable to assume that biorefineries are needed to achieve a sustainable energy sector in the long-term time perspective beyond the time perspective of this thesis, as CCS is considered to be a bridging system.

CO_2 capture is an end-of-pipe solution and is not competing with a fuel-switch from fossil fuel to microalgae. Therefore, the two measures could be implemented without mutual disruption, although the two processes cannot use the same excess heat. In the future, the major fraction of the production from the oil refinery could come from biomass-based processes (e.g., gasification, Fischer–Tropsch diesel, algae-based biofuels) rather than oil refinery processes. In that case, the amount of available excess heat would change and new case studies would have to be performed to identify a suitable absorbent for the CO_2 capture process. The CO_2 capture plant might also change in size according to the heat availability, since even if the oil refinery processes might be partially based on renewables, the opportunity for biomass-based CCS remains. Energy efficiency measures would also alter the availability of excess heat. As pointed out in Section 3.1.2, there is a potential 210 MW associated with heat integration, 20% of which is estimated to be economically feasible. The generic approach presented in Section 5.1.1 is therefore an important tool for deciding which absorbents are suitable. As the refinery becomes more efficient, the high-temperature sources of heat would probably be utilised first. This further underscores the importance of being able to decrease the stripper reboiler temperature, as sources with large amounts of low-temperature heat would persist.

If both CO_2 capture and any type of fuel switch from fossil to biomass are to be carried out, it is very important that policy changes are implemented that enable the industrial sector to count biomass CO_2 as being equal to fossil carbon. Such a policy framework is not in place today.

The remaining heat demand of all the processes after heat integration or of all the processes when considering stand-alone units, could be supplied using a CHP unit. As the generated

electricity would replace the build margin electricity, the CO_2 balance would be affected. In the New Policy scenario, the electricity generated from the CHP unit would replace coal-based electricity, which would result in a greater impact on the CO_2 balance than that seen in the 450 ppm scenario. Throughout this thesis, however, the use of heat pumps (CO_2 capture) and heat-only boilers (algae-based biofuel) is assumed.

7 Main conclusions

In this chapter the main conclusions drawn in the appended papers are presented.

It is clear that a very large algae-based biorefinery would need be constructed to achieve a reduction in CO_2 emissions similar to that obtained with CCS, even if only excess heat would be used to drive the CO_2 capture process. In the most promising case, a reduction of approximately 1 kt_{CO2}/y in CO_2 emissions per MW_{algae} installed capacity could be achieved. The refinery emits 1800 kt_{CO2}/y, and by utilising excess heat for CO_2 capture, a reduction of approximately 800 kt_{CO2}/y can be achieved.

In the case study refinery, it was possible to extract 90% of the full excess heat potential at 155°C when replacing just 30 heat exchangers. For full excess heat potential utilisation, over 100 heat exchangers would have to be replaced. At 120°C and 90°C, the extracted amounts of excess heat were decreased to 85% and 80%, respectively. The cost for the heat collecting system constitutes a minor expense relative to that of the CO_2 capture plant.

Under the assumptions made in this thesis, MEA is more suitable for CO_2 capture in industrial applications than ammonia when only excess heat is used to meet the heat demand of the stripper reboiler. This is due to the large amounts of heat available at just below LP steam condensate temperature. MEA captures more CO_2 at the lowest temperature investigated in this thesis (90°C), while ammonia has an optimal temperature for maximum CO_2 capture that varies but that never reaches the lower boundary of the temperature interval investigated.

It is possible to utilise low-cost excess heat to make post-combustion CO_2 capture feasible at an oil refinery in a future that involves strong climate mitigation policies. However, the difference in specific costs (€/t_{CO2}) between the cases that employ a temperature in the stripper reboiler of 90°C or 120°C are small. Due to the decreased operational costs when using excess heat, capital costs become increasingly important.

If heat integration between the MEA process and another industrial process is implemented, the increase in heat demand when the temperature in the stripper reboiler decreases is to some extent compensated for, since normally, more excess heat is available at lower temperatures, thereby reducing the external energy demand for the CCS process. The benefit of capturing more CO_2 when decreasing the stripper reboiler temperature and thereby being able to use more excess heat, is largely cancelled out by the increased need for compression.

The increase in available excess heat between 130°C and 100°C ($T_{Reb.}+\Delta T_{system}$) does not have to be large to, from a maximum CO_2 capture rate perspective, motivate a change in stripper reboiler temperature from the standard 120°C to 90°C. However, from the economic perspective, the increase in excess heat would have to be larger than that in the case study refinery to motivate such a change in stripper reboiler temperature.

For algae-based biofuels, the choice of scenario (New Policy scenario or the 450 ppm scenario) is crucial. For microalgae, the choice of scenario largely dictates the carbon balance, with the New Policy scenario giving increased CO_2 emissions and the 450 ppm scenario giving reduced CO_2 emissions. For macroalgae, the reduction in CO_2 emissions is halved when the New Policy scenario rather than the 450 ppm scenario, for an integrated plant. Macroalgae represent a more robust choice, CO_2-wise, than microalgae. Hydrothermal liquefaction (HTL) based on a macroalgal feedstock is the only investigated route that results in an overall CO_2 reduction in both scenarios. The reason for this is the lower energy demands for harvesting and cultivation of macroalgae. Macroalgae also have the benefit of reducing eutrophication (not quantified in this thesis), which is likely to become an even greater problem in the future due to projected climate change.

Under the assumptions made in this thesis, algae-based biofuel production processes would benefit from being co-located with an oil refinery. In the microalgae case (where there is a need for industrial flue gases), the same applies for the cultivation process. For the lipid extraction route, heat integration appears to be more important than material integration. The heat demand of the lipid extraction route can be satisfied with the available excess heat from the oil refinery. In contrast to the lipid extraction route, material integration appears to be more important than heat integration for the HTL routes, although this depends largely on the high temperatures required for HTL. The temperature levels of the available heat from the oil refinery are not sufficient to lower significantly the external energy demand.

8 Future research

This chapter provides some suggestions for future research connected to the research fields in this thesis.

To ensure that the specific heat demand is not highly dependent on the loading, a study would have to optimize the loading for each temperature.

As the investigation of generic amounts of excess heat show, it is beneficial to decrease the temperature for both the ammonia process and for the MEA process. Hence, there is a need for low-temperature amines that can capture CO_2 at atmospheric pressure (or preferable elevated pressures) for industrial applications with access to excess heat.

The use of more advanced strippers and absorbers, such as multipressure strippers and absorber with intercooling, would have to be investigated. Although multipressure stripping heavily increases electricity use, it can be of significance if using excess heat because the heat demand is lower.

This thesis has shown how the future hydrogen production technology affects the efficiency of the algae-based biofuel processes. Future research should show the most efficient, both energy-wise and CO_2-wise, for hydrogen production based on a number of scenarios.

As the nutrient balance is such an important parameter for the algae-based biofuel (and indeed all algae cultivation) nutrient recycling would be an interesting field for further study. Nutrient recycling is of importance if cultivating microalgae so that the nutrients will be in available form for uptake when re-circulated. Furthermore, nutrient recycling is also important when cultivating macroalgae so that the nutrients could be used in farming, reducing the need for artificial fertilizers.

A more thorough comparison between land-based and ocean-based cultivation predicated on experimental work is needed to see which of them that give the best yield. Research on how to reduce the energy input of cultivation and harvesting of microalgae is needed.

A legal framework for marine-based cultivation should be developed. If algae-based energy is implemented on a large scale there have to be a clear framework governing this.

List of abbreviations

ΔT_{min}	Minimum allowed temperature difference in a heat exchanger
ΔT_{system}	The minimum allowed temperature difference between the refinery process streams and the integrated process
450 (in tables and figures)	IEA:s 450 ppm scenario
CAPEX	Capital expenditures
CCS	Carbon capture and storage
CHP	Combined heat and power
CO_2 emissions	CO_2-equivalent emissions
FAME	Fatty acid methyl ester
FCC	Fluidized catalytic cracker
IEA	International Energy Agency
HEN	Heat exchanger network
HP	Heat pump
HX	Heat exchanger
LCA	Life cycle assessment/analysis
MEA	Monoethanolamine
MVR	Mechanical vapour recompression heat pump
NB	Natural gas boiler
NGCC	Natural gas combined cycle
NH_3	Ammonia
NP	IEA:s New Policy scenario
OPEX	Operational expenditures
SMHI	Swedish Meteorological and Hydrological Institute
$T_{Reb.}$	Temperature in the stripper reboiler
WEO	World Energy Outlook
WWT	Wastewater treatment
WWTP	Wastewater treatment plant

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Acknowledgements

This project has been part of the Energy Systems Programme, which is financed by the Swedish Energy Agency. Additional funding has been provided by: *the Preem – Chalmers co-operation*, which is financed by Preem AB.

The road to my PhD has at times been both winding and strewn with thorns, but there have been some people that picked me up when I was starting to feel like Sisyphus. I cannot thank you all individually, but you know who you are.

I would like to thank my supervisor Thore Berntsson for the discussions and support. And for the remarkable ability to pick up a piece of paper you have never seen before and immediately figure out how to draw conclusions from it. We might have disagreed on cultural expression forms (theatre or opera, 3-5 minute-songs vs endless symphonies by Sibelius, pop art or impressionism) but at least we agree on fado.

Per-Åke, thank you for always pointing out that no one understands what I am writing and that I therefore should be more clear. Also for widening my gastronomic perspectives with constant tips on where to find the best food when I go somewhere and making me try oysters for the first time.

Stefan, thanks for helping me with my last paper which turned out to be somewhat of a nightmare. You never lost hope (like I did) and for that I am grateful.

Fredrik and Henrik, thank you for your contribution on ammonia modelling and the fruitful discussions on what later became **Paper II**.

Thank you Eva and Joakim for the discussion regarding algae.

Thank you to the past colleagues in the Division of Energy Systems and Technologies and VoM, for fika and a good atmosphere during my time at the division. Anders, thank you for always helping me out in MatLab. Calculations aside, my figures would all look a mess without you. Thank you to my office mate Roman for all the train rides, discussions both on life in general and life at the division in particular.

The PES society, thank you for a year of fun! A special thank you to the members of the industrial consortium Sarah and Sandra.

To all my amateur psychologists (friends), thank you for helping me through this PhD. I don´t think I would have managed it all the way through without your love and support, wherever you (and I) have been in the world.

A thank you to all the wonderful staff at Sahlgrenska Universitetssjukhuset. I cannot thank you enough.

And last I would like to thank my family. My mum Eva, you are the best support I can have when I am freaking out, and when I´m going through a rough period in life. My dad Kenneth for always being there, ready to do everything in his power to make my life easier. My sister Elvira, with whom I can discuss life in academia in general and as a PhD student specifically; who understands the many obstacles that you have to pass but also the joy of it all. My brother Rasmus, who has proven that if you put your mind to it you can achieve almost anything, which has been a source of inspiration in the last year of my PhD. I love you all.